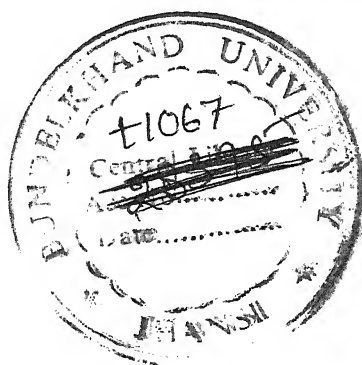# SYNTHESIS OF CHELATES AND STUDY OF BIOLOGICAL ACTIVITY OF SOME NEW BACTERIOSTATIC AGENTS

A THESIS
Submitted for the Degree of
DOCTOR OF PHILOSOPHY
in
CHEMISTRY

BUNDELKHAND UNIVERSITY
JHANSI

October 1991

Under the Supervision of
Dr. R. C. SAXENA
M. Sc , Ph. D.
Department of Chemistry
M. M. College, Modinagar
(201204)

Submitted by
DHRUV KUMAR AGARWAL
M. Sc.
Lecturer in Chemistry
Bipin Bihari College, JHANSI
(U. P.)

C E R T I F I C A T E

This is to certify that the thesis entitled "Synthesis of chelates and study of Biological activity of some new bacteriostatic agents" which is being submitted by Mr. Dhruv Kumar Agarwal Lecturer in chemistry Bipin Behari College, Jhansi for the award of Doctor of philosophy in chemistry of Bundelkhand University, Jhansi is a record of his own work under my supervision and guidance. The matter embodied in this thesis has not been submitted for the award of any other degree of any university.

Dr. R.C.Saxena
    Ph.D.(Roorkee)
Department of chemistry
M.M.College, Modinagar (201204)

Acknowledgements

It is my duty to express my sincere and grateful thanks to my supervisor Dr R.C. Saxena, Department of Chemistry M.M. College, Modinagar, whose valued guidance and critical evaluation of my work at considerable sacrifice of time and energy has helped me to achieve this level of accomplishment.

My greatful thanks are also due to Dr. S.C.Shrotri Principal, Prof. R.P.Khandelwal Head Chemistry Department, Dr. H.N.Singh Senior Lecturer in chemistry and Dr. R.K.Agarwal Head, Botany Department, Bipin Behari College, Jhansi for providing the necessary facilities.

My grateful thanks are also due to central Grass Land Research Institute, Jhansi and Central Drug Research Institute Lucknow for extending instrumental facilities.

Dhruv Kumar Agarwal
Lecturer in chemistry
Bipin Bihari College, Jhansi.

CONTENTS

CHAPTER--1

GENERAL INTRODUCTION

Schiff bases referred to as azomethines, anils or imines, constitute an important class of nitrogen donor ligands. These are the condensation products of primary amines with corbonyl compound (both aldehydes and ketones) and characterzed by the structure, RR'C =NR" where RR'C = represents an aldhyde or ketone residue and > N-R" represents the amino residue of a primary amine. In recent years, their complexes with metals and non-metal have been amongst the most widely studied co-ordination compounds on account of the stereochemical significance as well as agri- cultural and industrial applications of the ligands as well as their derivatives. The development in the field of bioinorganic chemistry have further stimulated interest in the design and preparation of such ligands and these can produce similar geometric constrains as the prophyrins and corrins.

Schiff bases and their metal complexes find use as pigments and dye for cotton, wool, synthetic fibres and plastics. These have also been used as high temperature stabilizers, inhibitors against acid corrosion of metal and alloys, antiknocking agents burning rate modifiers and in photographic emulsions, and liquid crystel display composition.

out of emerging areas of biological applications their uses as fungicides, insecticides, algaecides, plant growth regulators, oxygen carries in biological system and antiviral, antituberculosis, antitumour and anticancer agents have been reported.

the involvement of inorganic metal-based compounds in cancer treatment was very limited untill the accidental discovery

of potent anticancer activity in certain platinum co-ordination compounds by Rosenburg and Vancomp in 1969 and this key discovery has opened up a new class of antitumour agents namely inorganic co-ordination complexes.

The synthesis of a variety of schiff base and allied derivatives (Semi carbazones, thio-semicarbazones, S-substituted dithiocarbazates and azines) of main group elements (boron, aluminium, indium, silicon, gallium, germanuim, arsenic and antimony) as well as transition and innertransition elements (lanthanons, titanium, zirconium, vanadium, niobium, tentalum and uranium) by some newer preparative method as well as their bioinorganic applications, have been described.

These new derivatives have been synthesised by the reaction of alkoxides or acetates of metals, metalloids and non-metal with such ligands in the medium of dry benzene and under absolutely dry conditions such reactions are quite facil and straight forward and result in the isolation of clean products in almost quantitative yields. it has also been possible to synthesize asymmetric type of derivatives having two different schiff base moietis in the same molecular or mixed type of derivatives with one of the ligand moieties being the schiff base and the other one being any other suitable ligand or even metallic derivatives in low valence states.

The organoboron complexes of schiff bases derived from s-benzyldithocarbazates, sulpha drugs,semicarbazones and thiosemicarbazones have been shown to inhibbit the growth of gram postive as wellas gram negative bacteria even at very low concentrations. The fungicidal activity of boron

thisosemicarbazone complexes is appreciably higher than the two well-known fungicides,hevistin and PCBN.the aluminum derivatives of sulphonamide imines have been found to be active against pathongenic bacteria.

The organosilicon dithio-carbazate derivatives have also been screened for their antibacterial and antifungal activity and these have been shown to inhibit the growth of gram positive bacteria only. a 100% inhibition of fugal growth at 1000 ppm conc. in the case of A. tenuis and C tunate fungus has been recorded.

The organotin derivatives of schiff bases derived from s-substituted dithiocarbazates have been tested as amoebicidal agents and the tributyltin compound, $Bu_3 sn - (F.C_6H_4. CH. N.N. CS. SCH_2 C_6 H_5)$ has been fount to be some thirty times more active than the well known drug, ametine. it has also been shown that intratesticular administration of di-n-butyltin (o -hydroxy -acetophenone s- methyldithiocarbazate) destroys the seminiferous tubules of testes and prevents the formation of sper-matozoa, thus making the mice not suitable for reproduction.

The reactions of lanthanon alkoxides with fluorinated schiff base have also been studied. the lanthanum derivatives of 1,1,1,trifulor - 2,4 pentanedioneimines have been shown to exhibit faily intense broad-band fluorescence in the range 5200-6100 A0 with the peak around 5600 A0 . the condensation of aromatics aldehydes or diketones with 2-aminoethanethiol, 2-iminopropanethiol or aminobenezenethiol results in the formation of cyclic products containing a thiazoline ring. however, in presence of metallic or non- metallic-ions, isomerisation of these ligands to their tautomeric schiff base form takes place. A

varietyof new thio-schiff base derivatives of boron, aluminium, germenium, tin, lead titanium, tentalum, vanadium, and iron have been synthesized.

Preparation and characterization of molecules containing polymetallic centres has evoked much interest in recent years due to their involvement in catalytic processes. The use of metalloboraxanes and stannoboranes as plastic stabilizers, bactericides, fungicides, lubricants and water repellents have also been described. The synthesis of several such derivatives has been successfully carried out.

The field of cordination chemistry of macrocylic ligands has undergone a spectacular growth during the last few years, since it has been recognized that may complexes containing synthetic macrocylic compound may serve as models for biologically important species, whichcontain metal ions in macrocyclic ligand enviornment. A synthetic copper (I) complex of a schiff base with two imidazole donors has been described as a model for hemocyanin and a variety of bonded alkyl derivatives of cobalt (III) with open and macrocyclic schiff bases have been studied as model for vitamin B12 . Thus, it becomes evident that the schiff base and allied derivatives of metals, metalloid as well as non- metals have great significances from the point of view of agriculture as well as medicine. With a better understanding of structure reactivity relationship, it would be design even more potent bioinorganic materials, which in the long run, would serve as new resource, materials for human well being.

Polymeric schiff bases, have been described by several

authors(1-4). These polymers were of low molecular weight with limited solubilities and showed good thermal stabilities when chelated with various metal.

Though considerable progrese has been made in the field of complexation of heavy metals ions particularly Sn (IV), Hg (II), Pb (IV) with molecules of biological importance (5-6) due to the various reasons like main festation of novel structural features abnormal megnetic properties and relevance to biological process. Schiff base complexes have been also studied by poddar and sarkar (7). Dutt & Hossain (8) prepared some schiff basess and studied their complexing behaviour towards heavy metal ions. The Cu(II) complexes of schiff bases derived from biguanide salicylaldehyde have been prepared by Bera at al(9). Study of these complexes has gained importance because of their biological significance and interesting and magnetic properties.

Some metal complexes of tridentate schiff base derived from 3-aldehydo-salicyclic acid and cyanoacetic acid hydrazide, reported by pandey and Likhar (10). The ligand used was preapared by the reported method (11-12). The ligand behaves as biprotonic. The schiff base coordinate as neutral molecule very rarely . The usual form being the deprotonated anions of schiff base. The metal comlexes of the tridentate O.N.N. usually exhibit interesting magnetic and strutural properties (13-15). The strategic disposition of the donor sites in many of such ligands forces the ions to dimerise or polymerises.

Acetyl acetone reacts with two mols of benzoyl hydrazide to provide rather unusual schiff base (16). The infra red evidence confirms that the ligand gets enolised and than deprotonated and thus function as quadridentate dibasic ONNO donor.

In recent years interesting complexes of metals of usual co-ordination numbers (17-20) polycentric (21) hydroxo (22) and protonated (23-24) nature have been reported. Singh & Tondon (25-26) also studied the reaction of antimony (iii) Isopropoxide with schiff bases.

Recently the importance of mixed ligand complexes in medicinal chemistry(27) and industrial chemistry(28) has lead to a large number of reports on the formation and stabilities of mixed ligand complexes. Synthesis of metal complexes having unusual co-ordination numbers through a process of mixed ligand has evoked a lot of interest in recent years. Several mixed ligand Pentacoordinated complex of Co(II), Ni(II) Cu(II) Zn(II) and Cd(II) have been reported, some mixed ligand complexes of Cu(II) and Ni(II), diketone with neutral heterodonor ligands have been also reported in the literature.

Biochemical and medicinal significance of simple Zn(II) complexes has been discussed by many workers (29-30) Benzofuran derivatives are well known as biological and pharmacologically important compounds.

Using potentiometric technique Saxena and Coworkers (31-35) have carried out extensive studies on the complexation of Thiols with several metals. Mixed imine and aliphatic diamine schiff base complexes derived from Salicylaldehyde, O-OH acetophenone and 2-OH--Naphthaldehyde have been reported with bipositive metal ions (36).Alanino hydroxomic acid an analogue of glycinohydroxamic acid has been found to undergo condensation with salicylaldehyde to form crystalline schiff base which acts is a tridenate chelating ligand.

The lanthanide complexes due to lack of significant involvement of 4f orbitals in the bond formation are in general stabilised by ligands having strong electronegative donor atoms. However, their reaction with schiff hases except for few reports and semicarbazones do not seem to have been studied so far. Some of the complexes show potential biological activity.

The importance of thiosemicarbazide and mercaptotriazoles in medicinal chemistry is well known. Thiosemicarbazide are reported to possess antibacterial, antifungal, antiviral, antidiabetic and insecticidal activities. Marcaptotriazoles are associated with antibacterial, antifungal, antiviral and Schistosomidical activities. The schiff bases derived from amino acids are known to play an important role in biological reactions. Schiff bases derived from vanillin and amino acids and their chelation with heavy metal ions in ethanolic solution has been studied potentio-metrically and the Entropy change observed in order of stability (37) as Fe(III),> Cu(II),> Ni(II) Co(II) > and Mn(II).

Schiff bases derived from sulphoniamide are reported to be bacteriostatic. Amongst the azomethine derivatives of hydrazine and substituted hydrazines(38-39) those having > C=NNH2 moiety have been comparatively less investigated in term of their chelating ability(40). Amino acids containing active - NH2 and - COOH groups have several useful applications in biological, medicinal and allied fields are well known for the formation of complexes with metals. Their ready synthesis and myriad properties have contributed greatly to their popularity and to the study of biological systems.

Phenetsal a drug of vital importance form metal ion complexes(41-42). The siginficant studies reported in the literature are on the transitional metal ion complexes of amino acids because of their biological interest(43). Such studies have also been made on the chelates of Polyamino acids of lanthanide (III) ions.

The ability of complexation of oxytetracycline with heavy metal ions have been used for the photometric(44-50) determination as the tetracycline group of antibiotics contains multi-functional groups in their molecules which are responsible for the formation of several complexes with different metal ions(51). Some reports appears on the schiff base complexes of organotin(IV) halides contain in their neutral forms. Cancer formation and its inhibitation both involve chelation, Carcinogenic metals are generally transition metals, which have pronounced tendency for chelation and are associated with Vitamines, Proteins, and Nucleicacids. Chakraworthi, Tiwari and Sharma (52-54) reported chelate formation of the two most common and widely used penicillins (Penicillin-G and Penicillin V) with some tervalent carcinogenic metal ions eg Fe(III), Cr(III) and Al(III) using calvin-Bjerrum's PH-Titration Technique as adopted by Irving and Rossotti. The maximum value of n reaches ~ 2 in every case indicating formation of ML1 and ML2 complexes only. This suggested that two co-ordination position remain unoccupied with the expected octahedral geometry of the complexes which may be utilised for combination with tissues.

It has been reported that a Drug show increased activity when used in the form of their metal complexes and a number of

metal chelates inhibits tumour growth are used in the treatment of cancer also. A ligand Isonicotinic acid hydrazide which is an important anti-tubercular drug has been used in the complex formation, certain other hydrazides varying co-ordination sites for the metal ions have been studied by the earlier workers. A large number of hydrazides and hydrazones have been tested as antibacteial, antiviral and antitubercular agents(55-58). More recently interest has been growing in the synthesis and study of Physiological effects of hydrazides and some biologically active aminoacids including Tyrosine in relation to their cytostatic effect (59). In many cases an increase in the cytoctatic effects of the hydrazide is observed when it is complexed with a transitional metal ion. Bontcher and co-workers (60) have recently reported the synthesis and structural studies of Cu (II) complex of aspartic and glumatic acid hydrazides. Agarwal, rao and sahay (61) extended these studies to transitional metal complexes of a series of aminoacid hydrazides and their deivetives. The probable structures of complexes have been assigned and various ligand field and nephelauxetic parameters have been evaluated. Salicylate complexes of many chelates including those of transitional metal have been reported by Mehlotra (62). But most of these studies have been carried out in solution. In solid state conflicting results have been reported.

A recent communication by Junean et.al (63) on some aryl sulphonyl hydrazones derived from various heterocycles prepared by different methods, (64-70). Arylsulfonyl hydrazones of 2-furfuraldehyde and S-Nitroso furfural-dehyde have been reported

to possess antibacterial activity and (71) are also useful as anticoccidial agent (72) in poultry.

OBJECT AND SCOPE:-

Prompted from the above, it was found interesting and useful to synthesise potential ligands and to study their complexes with transition metals. The present studies have been initiated in this direction, with particular emphasis to determine the oxidation state, coordination number, the stereo chemistery and the presence or absence of distortion with this in view, some ligands namely p-chloro-Benzal thiosemi carbazone 2:5 dimethoxy phenyl glyoxal thiosemi carbazone, 4-p-methoxy phenyl thiosemi crbazone of 2.5 dimethoxy phenyl glyoxal, α-N-methyl-S-Benzyl-β-N- (2.5 dimethoxy phenyl glyoxal) methylene – dithiocarbazate, α-N-Me-S-Benzyl-β-N (2-Hydroxy-5-carboxy phenyl glyoxal) methylene dithiocarbazate, α-N-Methyl-S-Benzyl-β-N (2-amino – Benzophenone) methylene-dithiocarbazate, 5- Methoxy Salicylidene-0-amino -Benzophenone and 5- chloro- Salicylidene-0-amino – Benzophenone have been chosen. These ligands contain azomethine nitrogen Thioketone sulphur , Ketonic oxygen and phenolic hydroxyl group for chelation. some of these compounds are biologically active. The present investigations have been carried out by isolating the metal chelates of the above said ligands with Iron (III), Copper (II), Manganese (II), Uranyl (II) Nickel (II), Cobalt (II), Vanadyl (II), Chromium (III) Manganese (III) and cobalt (III) metal ions in solid state.

The metal complexes have been characterised by elemental, analysis magnetic suseptipility, electronic and vibrational spectral measurements.

Besides studying the stero chemical aspects of the chelates isolated the present work can further be extended in Mossbauer Spectral studies of iron (II) and iron (III) chelates for the elucidation of bonding in the complexes. Isolation of low valency state metal complexes, measurement of electronic spectra in polarised light and X-ray absorption spectral studies for elucidating the symmetry, about coordination sphare, nature and length of metal- ligand bonds.

LITERATURE REVIEW ON

MAGNETIC MEASUREMENTS

The magnetic studies has been utilised for many years as one of the most powerful techniques for predicting the type of bond sterochemistry and the oxidation state in the metal complexes. In the measurement of effective magnetic moment the donor set or the chromophore present in the ligand is responsible to a considerable extent in deciding the spin space of the metal ion i.e whether it is in high or in low spin or in intermediate State.

The magnetic prperties of complexes are frequently discussed in terms of quantity called the "magnetic moment" ueff rather than of the susceptibility. The magnetic moment is realated to the susceptibility.

$$\mu eff = (3K/N\beta 2)1/2 \ (nAT)1/2$$
$$= 2.828 \ (nA.T)1/2$$

where N-is Avogadro's number.

The d-d electrons are influenced by the ligand fields, magnetic behaviour is changed upon the incorporation of metal ions into complexes with the presence of ligand fields some of the orbitals used their degeneracy. It is because of this

behaviour the angular momentum consequently magnetic moment of the complexes is fairly explained with the second order effect calculated by the equation-

$$xg=N\beta \ 2/10D\sqrt{}$$

where N is the avogadro's number

$\beta-$ is the Bohr Magneton.

Some workers successfully explained the anamalous magnetic behaviour and then variation with temperature. The low magnetic moment value for the chloride (4.52 BM) and the nitrate (4.62 BM) complex suggest that they may have an orbital singlet ground state with a distorted octahedral environment (73). The ueff value of (2.0 B.M.) is well with in the range reported for spin paired octahedral complexes of Fe (III) (74-75). This indicate oxidation of Fe(II) into Fe (III) during isolation. Conclusion that Fe(II) is oxidised to Fe (III) is supported by electronic and infarared spectra of the complexes. However, the high value of magnetic moment in the nickel complexes indicates large orbital contribution (76). Low spin cobalt (II) complexes possess the magnetic moment (1.9BM) at room temperature which is in between for the two spin states and such intermediate values, can arise due to any of the following mechanisms (a) partial oxidation of Co (II) into Co (III) (b) antiferromagnetic exchange interactions c) equilibrium between the thermally assescible 2Eg and 4T2g states i.e 4T2g == 2Eg

In recent years there has been considerable interest in the magnetic exchange behaviour of transitional metal complexes (77-78). But majority of these studies have centered around the S=1/2 systems and relatively less attention has been paid to the S=1 and S=3/2 systems. Shah (79) et.al. isolated few complexes of

Ni (II) Fe(III) and Cr (III). The magnetic moment for ths Cr(III) complexes might be due to positive spin orbit coupling and small magnetic anisotropy irrespective of the nature of the bonding involved (80). The slightly higher value of ueff for the compound may be due to ferromagnetic impurity. Sahoo amd Mohapatara (81) noted in trnsition metal cluster complexes the magnetic moment of the paramagnetic Co (II) of the type (Co2 L2 X4) (where X=cl, Br, no3, and SCN) lie in the range (4-4.6 Bm) synthesis and characterisation of chelates of trivalent rare earths metals La, Pr, Nd, Sm, Gd, Ho, Er and Yb with schiff base, biacetyl bis (benzoylhydrazone)have been reported by the physico-chemical methods. The magnetic moment of all the complexes observed at room temperature show a very little deviation from von-vleck values(83) indicating as expected that 4f electrons are not involve in bond formation in these complexes. Mehrotra (84) reported the magnetic studies of many di-and trivalent metal ions, and found that copper alkoxides show a lowering in the value with decrease in temperature which suggests entiferromagnetic exchange interction between copper pairs in all these alkoxides (85) based on infinite chains of methoxy bridged copper atoms rather than layer type structure suggested earlier. The values of exchange coupling constatnt (J) in these alkoxides have been calculated. Oxovandium (IV) complexes has a magnetic moment of 1.7 B M which is close to the spin only value of (1.73 B.M.) expected for 3d complexes when the orbital contribution is completely quenched.

On the basis of magnetic suspectibilities at varying temperature the Fe (III) complexes withseveral quadridentate schiff's base were classified into four type (i) High spin

(S-5/2)(ii) Low spin (S=1/2)(III) intermediate spin (S=3/2) and (IV) crossover complexes. The last of which have a ligand field strength near crossover point of high spin and low spin types.

The diamagnetic behaviour of Co(II) complexes is rather unusual though not known (86-87). The cobalt (II) being a d7 system its complex should show paramagnetism either equivalent to three unpaired electrons (octahedral and tetrahedral geometry or equivalent to one unpaired electron (square planar geometry The observed diamagnetism of the Co (III) complex indicates spin pairing which could take place by the formation of bond between two cabalt ions with ligand molecules in the square planar geometry.

Iron (III) is known to form high spin (S=5/2) low spin (S=1/2) and inermediate spin (S=3/2) complexes under the influence of different ligand field. Spin cross over phenomenon is usualy observed with the iron (iii) compounds.

The low spin compounds give rise to the 2T 2g term and the temperature dependent magnetic moment is a function of spin-coupling parameter. the magnetic moment value is expected to be above spin only value (1.73 B.M) and less than about (2.5 B.M)(88). The excess over the value for one unpiared electron (1.73 B.M.) found for the complexes can be attributed to spin orbit coupling (89-90).

The Ni(II) complexes (91) of aryl substituted ligands show slight paramagnetism (0.5-0.7 BM) amd are assumed to be square planar. The slight paramagnetism observed could be due to (i) equlilbria between square planar and tatrahedral structures or (ii) the proximity of triplet 3Eg state to the groun state A1g for a square planar complexes or (iii) temperature

indepandent paramagnetism (92-93).

Although there have been considerable interest in co-ordination compounds of schiff bases with the 4d0 ion dioxomolybendum(94-95) (VI) comparatively very little has appeared on co-ordination compounds of schiff bases with th 5d0 ion dioxotungsten (VI)(96-98).Only two reports dealing with a few dioxotungsten (VI) co-ordination compounds of schiff bases have appeared in the literature (99).

The room temperature magnetic moment values of the trans and bis-cobalt (ii) complexes fall in the range (4.65- 5.01 B.M). The values in most cases are in good agreement with those (4.8-5.2 B.M) observed for most of the high spin octahedral cobalt(II) complexes (100). A lower value in some cases may be indicative (101) of a spin-state equilibrium between 4Tig & 2Eg States suggesting that the over all ligand field in the complex species is close to the cross over region of 3d7 cobalt (II) ion (102).

The chemistry of oxovanadium (IV) is of interest from chemical structural and biological point of view (103-107). The observed magnetic moment of six co-ordinated oxovanadium (IV) complex lie in the range (1.6-1.8 B.M.) close to the spin only value of a d1 - system (108). The complex [$VO(C2O4)(N-N$] exhibit the magnetic moment in the range (1.50-1.56 B.M). The low value of magnetic moment of the complex with (N-N) ligands and also lowering of V (Vo) mode in the I.R.spectra are indicative of the existence of V=0...... chain.

ELECTRONIC SPECTRAL STUDIES:-

Electronic spectra has been used in the past in assigning tetrahedral square planar and octahedral geometries as well as the polymetric intramolecular linkages. But it has been observed

that it may be used in number of ways to elucidate the structure of the complexes. The Spectral investigations of transitional metal complexes find wide application in terms of energy level schemes and chemical bonding which is the basis for consideration of many problems of the structure of the metal complexes.

Schiff base 2-salicylideneimino, 5-Mercapto-1.3.4-thiadiazole shows an electronic spectrum of an intense band at 260 nm (38460 cm-1) and a comparatively weaker band at 300 nm (33-330 cm-1). The high intensity of 260 nm band suggest it to be due to (d-d) transitions. The tetragonal cu(ii) complexes involves three transitions viz 2 B1g---> 2B2g, 2B1g---> 2Eg and 2B1g--->2 A1g. But bands due to these transitions usually overlap to give one bread absorption band (109) square planar complexes have complex broad band at relatively higher frequencies16000cm-1 The regular tetrahedral complexes of Cu(II) show no d-d absorption band in the region 10000-20000 cm-1.

The octahedral Cr (III) complexes axhibits bands at 263,405 and 585 nm assignable to the transitions (110).

4A2g(F)---> 4Tig(P) 4 1g (F) and 4T2g (F) respectively.

Many tetrahedral complexes of Fe (ii) are known to exhibits a broad, sometimes split band in the infrared region near 4000-6000 Cm-1 attributed to the ST2--->5E, transition. The electronic spectra of low spin Fe (II) complexes exhibit principal spin allowed bands corresponding to the transition 1A2g---> 1Tig 1T2g excited States.

The electronic spectra of Co(II) complexes give two d-d-transition bands in 5480-5800 and 6350-7690 Cm-1 regions and a

pair of bands in the 14660-16670 Cm-1 region. these may be assigned to 4B2<---4A2(F), .4E(F)<---4A2(F) and 4E(P)<---4A2(F) transitions. this is consistent with square pyramidel stereochimstry around Co(II) ion. The positions of the three d-d transition bands obtained around 24390,16810 and 14290 Cm-1 in the spectrum of oxovandium (V) complex could be assigned to the transitions dxy--->dz2, dxy--->dx2-y2 and dxy--->dxz, dyz respectively. These are indicative of square pyramidal geometry around vanadium.

In an octahedral Ni(ii) complexes three d-d transition band in the region 10101-10800, 16077-18180 and 25640-25660 Cm-1 assignable to the transitions 3A2g (V1)---3T2g,3A2g(V2)-->3T1g(f) and 3A2g--->3T 1g-(P) V3 respectively.

In the electronic absorption spectra of Pt (II) and Pd (II) Chelates one should expect three spin allowed and three spin forbidden bands. The weaker bands at 18600 Cm-1 in red colour (Pt complex) and at 19000 Cm-1 in brown colour are assigned to spin forbidden d-d- transitions, 2 Eg and 3A2g excited states respectively (111-112). The first spin allowed d-d transition B2g (xy--B1g (X2--Y2),1A1g--->1A2g is believed to occur at 25000 Cm-1 in ptcl4-2 and about 43000 Cm-1(113) in Pt(NH3)4+2 complexes. The very intense absorption band observed in the spectra at Ca 36000 Cm-1 is perhaps due to L--> M, charge transfer procees. In square planar dithio-oxalato complexes of Pt (II), Pd (II) very intense L---> M bands were observed at 36400 Cm-1 and 45000 Cm-1 respectively (114). The ground state for d6 Pt (IV) is 1A1g. The

ligand field transition eg. t5 2g<--t6 2g gives 3Tig 3,T2g and 1T1g and 1T2g as excited States in increasing order of energy. The electronic spectra of Pt (IV) complexes show absorption bands at 20000, 23500 and 29900 Cm-1 The bands at 20000 Cm-1 in Pt(IV) complexes are due to d-d transitions assigned to the singlet, triplet transition (115-116) 3 2g<--- 1Aig.

In the electronic spectra of the octahedral Pt (IV) complexes bands were obtained at ~ 660 ~ 550 and ~ 412 nm. which may be assigned to 2T2-->2E1, 2T2-->2T1 and 2T2--->4T1 transitions. The values are consistant with the earlier observations (117). Sharma et.al (118) reported Cr (III) complexes of maleanilic and Phthalanilic and their different substituted products. In the electronic spectral studies, the value of Racaha's interelectronic repulsion parameter B has been calculated by three different method as discussed by Konig (119). It is interesting to note that the calculated values of B and nephelauxetic ratio 35=B in complex B in free ion) depend significantly on the method adopted for their calculation. Metal complexes of schiff bases are studied extensively due to synthetic flexibility of these compound and their selectivity as well as sensitivity towards the Central metal atom. A number of review have been devoted to coordination chemistry of schiff base metal complexes (120-126). Three bands are observed in the electronic spectra (127) of Co (II) complexes which are due to spin allowed transition. A strong and intense band at ~26000 Cm-1 may be due to the ligand metal charge transfer.

Three weak bands around 720, 640 and 540 nm are observed in the electronic spectra of the octahedral Ni(II) comlexes which are assigned to the transitions 3A2g--> 3T2g (VI), 3A2(g)--> 3T1g(V2) and 3A2g--> 3T1g (P) (V3) respectively (128-129). The Ni (II) complexes of 3-aryl substituted ligands also exhibit three weak bands around 710, 680 & 550 nm which are assigned to the transitions, 1A1g-->1Eg 1Aig--> 1A2g and 1A1g-->1B1g respectively in the square planar symmetry (130. The reflectance spectra of Cr (iii) complexes (131) exhibit two bands at 435 and 465 nm. which are assigned to the transition 4A2g (F)---> 4T 1g (F) and 4A2g(F)---4T2g(F) respectively. These are charateristic of octahedral Cr(iii) complexes (132). The reflectance spectra of Fe (III) comlexes do not show any distinct band in the visible region. The Cu(II) complexes show two broad bands one around 670 nm due to 2B1g-->2A1g transition and another one around 540 nm due to 2B1g--->2B2g transition which may be indicative of square planar geometry (133) for Cu (II) comlexes.

INFRARED STUDIES:-

The infrared spectral studies are of an immence importance in the field of co-ordination Chemistry due to the several reasons:-

(a) In distinguishing the nature of various functional moieties present in the ligand as well as in its metal compounds.

(b) To ascertain the mode of co-ordination of the donor atoms with metals.

(c) To give an idea about the multiple bonding.

(d) To reveal isomerism and

(e) To ascertain the state of ligand whether free or bond and degree of molecular symmetry in the complex.

The absorption of light energy by organic compound in the visible and ultraviolet regions involves promotions of electron in o-and n-orbitals from the ground state to higher energy state. The infrared spectrum cannot commonly distinguish a pure sample from an impure sample. pure sample will have fairly sharp and well resolved absorption bands whereas the crude preparation do not have. The infrared spectrum can aid the progress of chemical reaction.

Sangal(134) et.al. studied the complexes of 2-quinoxaline - carboxamide and established their structure on the basis of IR studies they found that the ligand shows VC = 0 mode at 1705 CM-1 and two bands at 3410 and 3180 Cm-1 which can be assigned to stretching vibration of NH2 group. In all the complexes the (C=O) stretch shift to lower region by about 40-50 Cm-1 this indicate that Co-ordination occur through the oxygen atom of the amide(135-136) group. The infrared spectra of all the complexes of Nickel & cobalt are similar implying that the ligand

co-ordinates in same way in both the cases. The nitrate group show bands around 1380,1300 Cm-1 in addition to those at 1025-1075 and 830-835 Cm-1 indication of the semicoordination by nitrate group (137-138). The bands between 253 and 280 Cm-1 may be tentatively assigned as the V(RU-S) frequency (139). New bands appear in th Rhodium and Iridium derivatives around 345 and 330 Cm-1 can be tentatively assigned to V(Rh-S) and V(Ir-S) vibrations respectively which are absent in the spectra of free ligands. The ligands exhibit Thione == Thiol tautomerism show bands in the region 1560-1550, 1250, 1090, 1080 and 790-780 Cm-1 which are assigned in thioamide I,II,III and IV Vibrations respectively. These bands are not pure and have contributions from V(N-H),V(C-N),V(C-S) and V(C-H). The thioamide (IV) band has been found to have maximum V(C=S) contribution. This band shifts to lower frequency suggesting the co-ordination of the sulphur atom to the metal. The bands observed around 3540-3400 Cm-1 (V asy OH and VSY-O-H) and at 1600 Cm-1 (H-OH mode) may be attributed to the non-coordinated water(140). However, if the water-molecule also present as coordinated and lattice than two broad bands at ~3400 and 3525 Cm-1 would be observed in the complexes. The corresponding Cu(ii) complexes are, however, anhydrous and do not possess such nand.

The acetamido ligand displays a Keto==enol tautomerism

```
   H    O          OH
   |    ||          |
 - N -- C  ===  N= C -
```
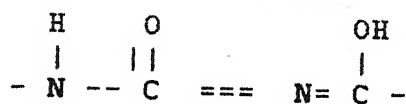
The mode of bonding of the metal ions with this ligand is either through Keto form or enol form. The copper complexes of the acetamido ligand displays bands at 3490 and 3350 Cm-1 indicating that this complex contains water of crystallisation

and has the -NH group in the amide structure. The strong band at 1690 Cm-1 for the anilide carbonyl group supports the co-ordination of the Keto form of the acetamido group to copper(142).

The effect of the hydroxy group ortho to Keto group was first noted in a 0-hydroxy acetophenone(143) and this was attributed to hydrogen bonding between the hydroxyl group and Ketogroup.

In the thiocyanate complexes V(C=N) is found around 2090-2105 Cm-1 region showing the presence of terminal N-bonded thiocyanate group. Nitrato complexes have the V1 and V4 bands in 1280 and 1410 Cm-1 region respectively. The difference V is of the oder of 130 Cm-1 suggestive of monodentate Nitrate coordination. The schiff base exhibits the V(C=0) mode at 1645 Cm-1 The absence of this band in the complexes indicates enolisation of the > C=0 group and subsequent coordination of oxygen atom. The complexes exhibit a new band at 1230-1245 Cm-1 due to the V(C-0) phenolic. A broad band at 3300-3400 Cm-1 confirms the presence of non coordinated OH group of the ligand. During the chelating behaviour of 2-Salicylideneimino -5 mercapto 1, 3, 4 - Thiadiazole a strong and broad band at ~3070 Cm-1 observed in the I.R. spectrum of the schiff base is characteristic of intramolecular hydrogen bonded phenolic OH vibration this is absent in the spectra of the metal complexes. The V(N-N) frequency remains unchanged in the spectra of the complexes ruled out the coordination of the ring nitrogen of the Thiadiazole moiety, instead the involvement of both the Sulphur atoms in co-ordination is indicated by the absence of VS-H vibration and batho-chromic shift of the V(C-S-C) vibration in

the spectra of the complexes.

The strong band in the region 1650-1350 Cm-1 are assigned to carboxylic stretching frequencies in the case of the oxalato complexes. The band at 1490, 1360, 1328, 795 and 498 Cm-1 for UO2(C204) IMZ and at 1505, 1335, 1310, 804 and 885 Cm-1 for UO2 (C204) PYz are characteristic for coordinated oxalato group (144). This suggest that in the complex the planar symmetrical configuration of the oxalate groups where they act as bridges between two UO2 ions in polymeric forms, is retained(145). Mehta et.al(146) reported dissociation constant of 2(N <-benzyl-2-hydroxy benzylidine imino) ethane sulphonic acid with heavy metal ions. All the complexes give one broad band in the region 3200-3230 Cm-1 due to VOH of the water molecules. The loss of water molecules relatively at high temperature (> 180) indicates that these are co-ordinated and not in a lattice field. In the spectra of uranium complexes two new bands at 900 and 970 cm-1 are assigned to Uo2 (II) ion, Usually two characteristic frequencies in the region 950-890 and 830-820 cm-1 are reported for Uo2 (II) in the metal chelates(147). Lowering of these frequencies in the uranium complexes is a clear indication for the involvement of oxygen of Uo2(II) in bonding. In the spectra of the 1:3 diazole complexes the N-H bonding and stretching frequencies which occur at ~1465 and ~3300 Cm-1 respectively, clearly show that 1:3-diazole and its derivative are coordinated through the tertiary nitrogen atom as confirmed by the reported X-ray structural studies(148).

The nitrate complexes [Cu(bzac)L2] No3 show a strong N-O stretching mode around 1350 Cm-1 (Vs) region and two inactive

deformation modes around 850 (V2) and 760 Cm-1 (V4). These indicate ionic nature of the nitrate ion having D3h(149-151) symmetry. The perchlorato-complexes display three sharp bands at~1100~1080 and ~1070 Cm-1 and another band at ~920 Cm-1 suggesting the coordinated behaviour of Clo4. The diagnostic IR band of the polyatomic anions indicate that the perchlorate group remains ionic in the trans-complexes (IR band at 1150 - 1060 Cm-1 (V3) and 620 Cm-1 (V4) are assigned to ionic perchlorate in Td Symmetry(152). The ionic nature of the BF4 group is ascertain by the appearance of a strong but very broad band in the region 1105-1035 Cm-1 (V3) mode of BF4 ion in Td symmetry(153).

The most characteristic feature of the I.R. spectrum of the [VO(acac)2] is the appearance of a sharp strong band at 995 Cm-1 (154-155) assignasble to (V=O) modes.

It is found that in the imidazole complexes bands occur at ~30,00 Cm-1 1570 Cm-1 and 1640-1650 Cm-1 (broad split) respectively. The broad band in the range 1640-1650 Cm-1 is probably due to the coupling of V(C=N) of the imidazoles and V as C=O of coordinated carboxylic group with the Vo(TV) ion Thus, the I.R. Spectra of these complexes support the bidentate coordination of imidazole molecule.

Schiff bases derived from aromatic diamines and mono or dicarboxyl compounds are multidentate ligands which can act in a variety of ways(156-157). In the far I.R. Spectra various new band observed are characteristic of V(M-N) or V(M-O) frequencies. The new band in palladium (II) complexes observed at 435-460 Cm-1 may be assigned to V(Pd-N) while those observed at 410-465 Cm-1 may be assigned to V(Pd-O) (enolic) vibrations(158-159) on steric

ground it can be said that these schiff bases can not form monomeric structures. On the basis of previous work in this field(160-162) these complexes may be present in dimeric form.

Infrared spectral bands due to pyridine in spectra of complexes are observed at high positions compared to the corresponding band in the spectrum of free pyridine (observed between 900 and 1215 Cm-1) similar bands also observed earlier by Green wood and wade(163) in substituted pyridine complexes.

Two strong bands are observed at 2900 and 2500 Cm-1 for the schiff base and its complex can be attributed to H-bonded O-H of carboxylic group. Complexes of benzylhydrazine (BH) and isonicotinoylhydrazine (INH) with Uranyl sulphate and oxalate have been isolated and characeised on the basis of infrared and Raman spectral data. I.R.Spectra indicate that BH and INH acts as neutral bi-and Tri-dentate ligands coordinating through >C=O, - NH2 (-CONH2) and pyridine nitrogen respectively. Sulphato and oxalato groups acts as bridging bidentate ligands respectively. I.R. and Raman spectral data indicate that all ligand atoms are arranged in the equatorial plane around the Uo2(II) group which maintains its linearity in all the complexes. A strong band at about 852 Cm-1, suggests that the linearity of the OUO group is maintained in these complexes. The absorption band of medium intensity at 910 Cm-1 in BH is masked by strong absorption at 925-905 Cm-1 due to V3 vibrations the doubly degenerate OUO bending mode V2 is observed between 255 and 235 Cm-1 in low frequency I.R.spectra of these complexes.

The free oxalate group belongs to D2H symmetry and shows V as C=O and Vs C=O modes at 1640 and 1335,1316 Cm-1 respectively. In

compounds where the oxalato group covalently bonded through four (bridging) oxygen atom the symmetry remains unchanged but when the oxalato group is covalently bonded through two oxygen atoms (Chelating or bridging) the asymmetry is changed to C2v (chelation) or to C2h (bridging) respectively.

2:4-dihydroxy benzophenone semicarbazone and thiosemicar-bazones as new chromogenic reagents for the rapid spectro photometric determination of copper was used by Reddy et.al(164). Coordination through ketonic oxygen and thioketo-sulphur is corroborated by the appearance of bands at 483 and 325 Cm-1 which may be assigned(165-166) to V(Cu-O) and V(Cu-S) in copper complexes. Similarly V(Cu-N) bands are observed at 599 and 563 Cm-1 in copper complexes of DBPS and DBPT respectively.

The I.R.Spectra of isonitroso complexes do not exhibit any bands at 1195 (C-H) and 795 Cm-1 (C-H) indicating that substitution has occured. The band occuring in the range 1640-1680 Cm-1 shows the presence of un-coordinated carbonyl group (167).The band in the range 1610-1630 is indicative of>C=N-group, while the band around 1600 Cm-1 indicates coordinated carbonyl group. The band occuring at 1180(-N=O) and 1140 Cm-1 V(N-O) suggest that both O and N bonded moieties are present in the same molecule. The isonitrosobenz-oylacetone complexes exhibits similar I.R.characteistics.

The characteristic frequencies below 700 Cm-1 generally have following aspects:

(a) They involve mainly skeletal bonding vibrations for light atoms and stretching vibrations for heavy atoms.

(b) The mass is usually large but bot always.

(c) The force constant is usually small.

(d) The vibrations are often associated with three or more atoms.

(e) They are influenced more by neighbouring groups and may occur over a wide frequency range.

CHARACTERISTICS FREQUENCIES ABOVE 700 Cm-1

(a) They involve mainly stretching vibrations except for vibrations involving hydrogen.

(b) The mass of single atom is usually small.

(c) The force constant between the atoms is usually large.

(d) They are often localised characteristic frequencies and may not be effected too much by neighbouring groups.

Halogen and Nitrogen bases have a tendency to form bridges resulting in polymeric forms. In general bridging (M-X) (X=Cl,Br,I) stretching frequencies are lower than terminal (M-X) stretching frequencies. Far infrared spectra of metal chelates is most useful for differentiating between various stereochemistries i.e. octahedral, planar geometry, Trigonal Bipyramidal and Tetragonally bipyramid. Plasticity of the coordination sphere of the metal complexes provides the types of bonding, stereochemical distortion, bond angle, bond lengths, micro geometry and micro-symmetry.

CHAPTER I

REFERENCES

1. Marvel C.S. and Bonsignova P.V. -J. Am.Chem.Soc.81(1959) 2668.

2. Marvel C.S. & Tarkoy N. -J. Am.Chem.Soc.79(1957) 6000;80 (1958)832.

3. Deconene C & Teyssie P.H. -J.Polym-Sci 57 (1962) 121.

4. S.K.Srivastova, R.B.Pathak and S.C.Bahel Jour. Ind. Chem.Soc.66, 210(1989).

5. S.L.Chadha and Kamini Uppal -Ind. Jour. of Chem. 29A(1990)80.

6. R.H.Holm and M.J.D.connev -Prog.Inorg.Chem. 14(1971)253.

7. S.N.Poddar and A.K.Sarkar -J.Ind.Chem.Soc. 45(1968)11,979.

8. R.L.Dutta and M.N.Hossain -Ind.J.Chem. 23A (1984) 30.

9. Y.D.Kulkarni,Nisha Saxsena and O.P.Srivastava -Ind.Jour. of Chem. 29A (1990) 77.

10. K.K.Pandey and J.V.Likhar -Jour.Ind.Chem.Soc.57 1(1980).

11. S.L.Chadda and Kamini Uppal -Ind.Jour. of Chem.29A(1990)80.

12. R.Faggani, R.J.Gillespie, C.Campana and J.W.Kolis -Jour. Chem. Soc. Chem. common(1987) 485.

13. W.E.Hatfield and R.Whyman -Transition metal Chem.(1960) 5,47.

14. T.N.Srivastava, P.C.Srivastava and R.Kumar -Ind. J.chem.21A (1982) 309.

15. A.K.M.M.Haque, S.E.Kabir, A.B.Kazi, K.Kundu, M.W.Miah and S.S.Ullah -Ind.Jour. of Chem. 29A(1990) 25.

16. R.L.Dutta and A.K.Sarkar -Ind.J.Chem. 19A(1980) 1180.

17. S.P.Tripathi, R.C.Sharma and G.K.Chaturvedi -Z anorg. Allg. Chem.(1980) 462,226.

18. L.C.Thompson and J.A.Loraas -Inorg.Chem.(1968) 2,89.

19. S.P.Tripathi, G.K.Chaturvedi and R.C.Sharma -J.Inst.Chem. (1980) 52,203.

20.   G.Andergg, P.Nageli, F.Mullar and G.Schwar Zenbak -Helv.Chim.
        Acta. (1959) 42,827.

21.   E.Brucher, R.Kiraly and I-Toth -Inorg. Nuclear, Chem.Lett
        (1976) 12,167.

22.   G.S.Malik, S.P.Singh and J.P.Tondon Z -Natur forsch (1977)326,
        426.

22(a). A.K.Mukherjee and R.Ashare -Chem.Rev; vol91, No1(1991)1.

23.   R.Kumar,   R.C.Sharma, and G.K.Chaturvedi -Mh.Chem.(1979)
        110,907.

24.   R.N.Kapoor, S.K.Mehrotra and V.S.Ray Purohit -J. Chin.Chem.
        Soc. (1977) 24,71.

25.   J.P.Tandon and O.P.Singh -Ind.J.chem. (1976) 14A, 709,
        R.Prasad,   Lallan Mishra   and U.C.Agarwal -Ind.J.Chem.30A
        (1991) 45.

26.   J.P.Tandon and O.P.Singh -Inorg.Chim. Acta (1976) 20,137.

27.   P.D.Hosten "Drug interaction" 3rd Edn. Henry Kimpton. Pub.
        London (1976).

28.   R.Breslow -Adv.Chem.Ser(1971) 100,21. D.S.Pandey, R.L.Mishra
        and U.C.Agarwal -Ind.J.Chem. 30A(1991) 41.

29.   B.L.Oser "Physiological Chemistry 4th Edn Tata MC Graw Hill
        Publishing Co., New Delhi -(1976) P.559.

30.   S.K.Bajaj and P.R.Sukla -J.Ind.Chem.Soc.(1980) 57,219. Shekhar
        Srivastava, Shradha Srivastava and A.Sharma -J.Ind.Chem.Soc.
        67(1990) 310.

31.   R.S.Saxena, K.C.Gupta and M.L.Mittal-cand.J.Chem.(1968)46,311.

32.   R.S.Saxena and S.S.Sheelawant-J.Inorg.Nucl.Chem.(1973)35,1383.

33.   R.S.Saxena and M.C.Saxena -J.Ind.Chem. Soc.(1976) 52,633.

34.   M.Calvin and N.C.Melchior -J.Amer Chem.Soc. (1948) 70,3270.

35.   J.Bjerrum "Metal Amine formation in aqueous solutions" P.Hasse
        and Sons copenhagen (1941).

36.   B.T.   Thaker and P.K.Bhattacharya -J.Inorg.Nucl. Chem. (1975)
        37.615; Ind.J.Chem.(1976) 37,615;J.Ind.Chem.Soc.(1975) 52.454.

37.   P.B.Chakrasvorti   and P.Khanna -Jour Ind.Chem.Soc.(1948)
        61.416.

38.   R.H.Holm.G.W.Everett and A.Chakarverthy -Prog.Inorg.Chem.
        (1966) 7.83.

39.   K.Dey -J.Sci.Ind.Res.(1974) 33,76;A.K.Dey, D.K.Dwivedi and
        B.V.Agarwal -Jour.Ind.Chem.Soc.67,1990) 339.

40.   V.J.Tyaga Raju et.el. -J.Ind.Chem.Soc. (1982) 59, 199.

41.   V.K.Jaitly and B.S.Pannu -Thermo Chim Acta (1983) 60,109.

42.   V.K.Jaitly,H.S.Hotha and B.S.Pannu-Thermo Chim Acta (1983)
        62.369.

43   Ev.Raju and H.B.Mathur -J.Inorg.Nucl.Chem.(1968) 30,   2181
        (1969) 31,425.

44.   T.T.Sakaguchi, M.Tomar. T.Yoshida H.Omura and H.Takasu -chem.
        Par. Bull (Tokyo) (1958) 6,1.

45.   D.R.Gupta, Kamaluddin and Sobha Naithani -J.Ind.Chem.Soc. 66
        (1989) 160.

46   Y.Apeloig, M.Karni and Z.Repport-J.Am.Chem.Soc.(1983)105,2784.

47.   S.Sen and V.Srivastava -J.Ind.Chem.Soc. 66 (1989) 166.

48.   R.N.Prasad and Mithlesh Jindal -Jour.Ind.Chem.Soc. 66 (1989)
        188.

49.   P.R.Shukla etal -Jour. Ind. Chem. Soc. 65 (1988) 663.

50.   P.R.Shukla etal -Ind. Jour. of Chem. 27A (1988) 1053.

51.   P.R.Shukla and N.Ahmad -Curr -Sci.(1988) 57,247.

52.   P.B.Chakrowarthi and A.Tiwari -J.Ind.Chem.Soc.(1980) 57.134.

53.   P.B.Chakrowarthi and A.Tiwari -J.Ind.Chem.Soc.(1980) 57.134.

54.   P.B.Chakrowarthi, A.Tiwari and H.N.Sharma -Jour.Ind.Chem.Soc.
      (1980) 57.268.

55.   W.Werner -J. Org. Chem. (1953) 18,1933.

56.   K.U.M.Prasad, B.H.Iyer and M.Sirsi -J. Ind. Chem. Soc. (1966)
      43. 784.

57.   S.S.Parmer and R.Kumar -J.Med. Chem. (1968) 11, 635.

58.   E.D.Taylor   and   W.L.Nobles -Jour.   Am.   Parm.   Association,
      Soci. (1960) 49,317.

59.   H.Barton,   J.Mokrosz and J.Bojarski -Tetrahedron Lett.(1982)
      23,20.

60   P.R.Bontchev,   M.Bonera,   M.Mitewa,   D.Mahandijev   and
      E.Golovinsky -J.Inorg.Nucl.Chem. 43(1981) 3163.

61.   R.C.Agarwal,   T.R.Rao and Mamta Sahay -Ind.   J.   Chem.   23A
      (1984) 214.

62.   R.C.Mehrotra and J.P.Tandon -J. Ind. Chem. Soc. (1961) 38,169.

63.   R.Junean,   S.Mitchell and G.Wolganott -J.   Pharm. Sci. (1979)
      68, 930.

64.   N.K.Vidya,   C.V.Reddy Sastry,   D.R.Sh.Dhar,   G.S.Thapar and
      G.S.Reddy Curr.   Sci.(1975) 4448,   J.Med.Chem.   (1977) 20,149,
      Ind.   J.   Chem. (1978) 1613, 704, Jour. Ind. Chem. Soc. (1980)
      57,1118.

65.   L.Friedman,   R.L.Little   and   W.R.Reichln   -Org.   Synth.
        Coll, Vol. 5, 1055.

66.   B.R.Havinale and I.B.Pujar -Jour. Ind. Chem. Soc. 65, 710
        (1988).

67.   R.C.Saxena, H.S.Verma, A.K.Katiyar and A.Paul -Jour. Ind.
        Chem. Soc. 60(1983) 84.

68.   C.R.Bera and G.P.Sen Gupta -J.   Ind.   Chem. Soc. (1987),
        64, 689.

69.   M.Ghandour,   H.Mansour and M.Khoday -J.   Ind. Chem. Soc.
        (1984) 61,862.

70.   M.C.Chakravorti and T.Gangopadhyay -J.   Ind.   Chem. Soc.
        (1987) 64, 573.

71.   H.Barton,   J.Bojarski   and J.Mokrosz -Tetrahedron   Lett.
        (1982), 23, 20.

72.   P.A.C.Dasaliva   and P.G.David -Bull.   Chem.   Soc.   Japan
        (1982), 55, 26, 73.

73.   A.B.P.Lever -Inorg. Chem. (1963) 2, 1162 (1965) 4, 1042.

74.   E.Kronkhe -Chem.   Ber - (1950) 83, 35; (1953), 86, 1132;
        (1954) 87, 1126, (1955) 88, 863.

75.   D.P.Singh and V.B.Rana -Jour.   Ind. Chem. Soc. 66 (1989)
        266.

76.   A.D.Damodaran,   F.M.Ichaporia and G.S.Rao -J. Ind. Chem.
        Soc. (1968) 45, 690.

77.   W.U.Malik,   R.Bembi and R.Singh -J.   Coord. Chem. (1983)
        12, 273.

78.   A.Kumar and L.K.Mishra -Jour.   Ind. Chem. Soc. 66 (1989)
        268.

79.   W.U.Malic,   P.N.Gupta and A.Raina -J.Ind. Chem. Soc.
        (1986) 63, 808.

80.   A.P.Cinsberg, R.C.Sherwood and E.J.Koubeck -J.Inorg.
        Nucl. Chem. (1967) 20,353.

81.   B.K.Mahapatra and B.Sahoo -Ind.Jour. of Chem. -21A, 376
        (1982).

82.   V.B.Rana,   D.P.Singh and M.P.Teotia - Ind.J.Chem.(1982)
        21A, 528.

83.   D.M.Yost, H.Russel and C.S.S.Garner -Rare earths elements
        and compounds (Wiley New York), 1947, Chap -2.

84.   R.C.Mehrotra -Jour. Ind. Chem. Soc. (1982) 59, 718.

85.   A.K.Yadav,   G.J.Mishra and S.P.S.Jadon -Jour. Ind. Chem.
        Soc. 65 (1990) Vol. 76.

86.   M.C.Saxena and S.N.Limaye -Jour. Ind. Chem. Soc. 66
        (1990) Vol. 76.

87.   L.K.Mishra and Kabita Das -Jour. Ind. Chem. Soc. 67
        (1990) 158.

88.   B.K.Patel and M.M.Patel -Jour. Ind. Chem. Soc. 67 (1990)
        186.

89.   S.P.Tandon,   Renu and A.M.Bhandari-J. Ind. Chem. Soc. 67
        (1990) 189.

90.   A.Earnshaw "Introduction Magneto Chem." Academic Press,
        New York (1966) P.34.

91.   L.D.Dave,   Cherian Mathew and Varughese oommen -Indian
        Journal of Chemistry (1986) 25A. PP 914-917.

92.   S.R.Saham Amitava Bagehi and Asutosh Das -Jour. Ind.
        Chem. Soc. 67 (1990) 234.

93.   R.K.Dubey and L.K.Mishra -Jour. Ind. Chem. Soc. 67 (1990)
        235.

94.   S.R.Saha   and A.Bagchi -Ind.   J.   Chem.   Sect.(A)
        1985, 24, 610.

95.   Hill W.E, Alabay N.M.C, Aulife C.A., M.C.Cullough F.P. &
        Razzoki, S.M. -Inorg. Chim.Acta 35(1979) 35, Rajan O.A,
        Adikari S. and Chakravarty. A -Indian. J.Chem.15A (1977)
        337; Rajan O.A. & Chakravorty A. -Inorg.Chem.20 (1981)
        660; Yamanouchik & Yamada S. -Inorg.Chim.Acta. 9(1974)
        83, Topich. -J.Inorg.Chem. 20(1981) 3704; Syamal A.&
        Kumar D.   -Transition Met.Chem.7(1982)   118;   Indian
        J.Chem.21A(1982) 534, Syamal A.& Maurya M.R. -Indian
        J.Chem.22A(1984) 950; Prabhakaran C.P. & Nair B.G. -
        Transition Met Chem. 8(1983) 368.

96. (a) Yamada S. -Coord.Chem. Rev. 1(1966) 415.

    (b) R.K.Patel and R.N.Patel -J.Ind.Chem.Soc. 67(1980) 238.

97.   Holm.R.H, Everett (Jr) G.W. & Chakravarty. A Prog.Inorg.
        Chem. 7(1966) 83.

98.   Curtis N.F. -Coord.Chem.Rev. 3(1968) 3.; V.P.Shedabalker,
        Amita Chaudhry and S.N.Bhatt -Ind.J.Chem.29A(1990) 171.

99.   Yamanouchi K.& Yamada S -Inorg.Chim.Acta -11(1974) 223;
        12 (1975) 9.

100.   Figgis B.N.& Lewis.J.Inorg. Chem. 6(1964) 37.; P.R.Shukla
        M.C.Sharma, M.Bhatt, Nihal Ahmad and S.K.Srivastava -Ind.
        Jour. of Chem. 29A (1990) 186.

101.(a) Walmsby J.A. & Tyree S.Y. -J.Am.Chem.Soc. 83(1961) 3770.

    (b) Bannister and Cotton F.A. -J.Am.Chem.Soc. 82(1960) 2276.

    (c) Y.Fanaber and Suqavo -J.Phys.Soc. Japan (1986) 68, 654.

102.   Lot A.N. -Inorg. Chem. 13 (1974) 667.

103.   Selbin -J. Chem. Rev. 65 (1965) 153; Minu Gupta, Jyoti Seth and U.C.Agarwal -Ind.Jour.of Chem. 29A(1990) 143.

104.   Stewart P.C. & Porte A.L. -J.Chem.Soc.Dalton Trans (1972) 1661.

105.   Pasquali, M.Marchetti F.Floriani C & Merlino S. -J.Chem. Soc. Dalton Trans.(1977) 139.; EL -Shahway A.S; Girgis, M.M and K.A.Idriss -Spectro Chim Acta 41A(1985) 1463.

106.   Mannis C.E. & Zipp A.P. -J.Inorg.Nucl.Chem.41(1979) 59.

107   Huddson T.G.F.Vanadium Toxicology & biological significance (Elsevier New York) 1964.

108.   Dutta R.L. & Sengupta G.P. -J.Indian Chem.Soc.49(1972) 919.

109.   Y.Nishida and S.Kida - coord. Chem.Rev. (1979) 27, 275.

110.   L.Pauling - nature of chemical bond cornell, Univ. Press. Ithaca, N.Y(1960

111.   D.S.Martin, M.A Ticker and A.J.Kassman- Inorg. Chem. (1965) 4 1682.

112.   H.Basch and H.B.Gray- Inorg. chem. (1967) 6, 365.

113.   J.P.Colleman and W.R.Roper- J.Amer Chem. Soc. (1965) 87, 4008.

114.   R.S.Nyholm and K.Vriaze- J. Inorg. Nucl.Chem (1962) 24, 5337.

115.   C.K.Jorgensen-J.Inorg. Nucl.Chem. (1962) 24, 1571.

116.   P.C.Srivastava and B.K.Banerjee- Acta chem.acad.Sci. Hung.(1978) 96, 259.

117.   A.H.Awaid   B.L.Martin   E.inn   and A.H.White-Inorg. Chem.(1969) B,210.

-36-

118. (a) C.L.Sharma R.S.Arya and S.S. Narri- J.Indian Chem. Soc.63 (1986) 267-269.

(b) P.S.Radha Krishnan and P. Indersenan (1990) 243

119. (a) E. Konig- Struct. bonding (1971) 9, 175.

(b) V. Giri and P. Indersenan- Polyhedron (1983) 2;578.

120. R.H.Holam. G.W. Everett, jr. and A. Chakravorti-Prog. Inorg. Chem. (1966) 7, 83.

121. (a) S.Yamada- Coord. Chem. Rev. (1966) 1,415.

(b) A.K.Mukherjee and S.K.Sanyal-Con.J.hem. (1986) 64, 717.

122. (a) S.Yamada- coord. Chem. Rev. (1967) 2, 83.

(b) S.K.Sanyal Chem. Edv. (1984) 1, 14.

123. R.H.Holm. and , M.J.Oconnor- Prog. Inorg Chem. (1971) 14, 241.

124. (a) M.A.Ali and S.E.Livingstone-coord. Chem. Rev (1974) 13, 101.

(b) K.Ganapathy and A.N.Palaniappan J. Ind. Chem. Soc. (1989) 66, 301.

125. (a) V.Casellato . M. Vidali and P.A.Vigato-coord. Chem. Rev. (1977) 23,37.

(b) B.C.Roy, C. Bondyopadhyay and M.B.Saha-J Ind. Chem. Soc. 67(1990) 264.

126. M.C.Golanka and Bartecki- coord chem Rev. (1979) 31, 251.

127. A.B.P.Lever "Inorganic electronic specto Scopy" Elsevier, Amsterdam (1968) P.212.

128. Bagdanov A.P., Zelentsov U.V. & Phadlko V.M.-Russ-J-Inorg. Chem. 10 (1977) 1417.

129. lever A.B.P. Inorganic Electronic Spectroscopy (Elsevier, New York) (1968) 341, 343.

130. (a) Calbertson Harry, Decius J.C & Bert E. Chersten-j Am. Chem Soc. 74 (1952) 4834.

(b) Shekhar srivastava, Shraddha Srivastava and Anjulata Harma- J. Ind. Chem Soc. 67(1990) 310.

131. K.K.Aravindakshan- Indian J Chem. Vol. 25A (1986) pp. 1052-1053.

132. Figgis B.N.-Introduction to ligand field (Interscience New York) (1964)

133. Weeks M.J. & Fackler J.P Inorg. chem. 7 (1968) 2548.

134. Sangal. A.B.Modak and A.K.Mudi- Ind. J. vhem (1981) Vol. 20A, 510.

135. R.Jagnnathan and Soundarajan- J Çoord.chem. 4 (1979)31.

136. M.Noji. Y. Kidani and H.Koike-Bull. chem. Soc. Japan (1975) 48, 2274

137. N.F.Curtis and Y.M.Curits-Inorg. Chem.(1965) 4,804,S.Srivastva. Sharadha Srivastva and A.Sharma-J.Ind. Chem. Soc 67 (1990) P 310.

138. D.S.Brown, B.G.A. Melson, B.O. Hathway, I.M. Proctan and A.A.G. Tomlinson-Chem.Commun.(1967) 366, D.K.Durvedi, B.V.-Agarwal and A.K.Dey- J. Ind. Chem. Soc. 67,339 (1990).

139. Oconur, J.D.Gilbert and G. wilkinson-J. Chem. Soc(A)(1969) 84.

140. P.A.Lacchesi and W.A.Gleson- J.Am.Chem.Soc.(1956) 78,1347.

141. R.C.Dass, M.K.Misra and S.K.Mohanty-Ind.J. Chem. (1981) 20A, 528.

142. H. Jaffe and M. Orchin- Theory and application of UV-Spectoscopy (John-Wiley, New York) 1962.

143. S.M.Saadesh, M.S.Lah and V.L.Pecraro - Inorg. Chem.30, P-8 (1991).

144. G.ondorbellt, I.Fragala and S.Giuffrida - J. Inorg. Nucl. Chem. (1975) 37, 1177.

145. G.S.Rao, S.C.Jain and M?S>Gill- Indian J. Chem. Sect A (1982) 21, 526. 145 (A) K.Mohan Rao, L. Mishra and U.C.Agarwal Ind. J. Chem. 27 A(1987) 755.

146. R.K.Mehta, Ashok Gahlot and Shobha Sharma- J. Ind. chem. Soc. 63, 198 (1986).

147. J.Selbin-Angew, Chem. (1966) S.712; M.westerhausen- Inorg. Chem. 30 (1991 P-96.

148. B.K.S.Lundberg- Acta Crystallogr (1966) 21, 901.

149. N.F.Curtis and Y.M.Curtis - inorg. Chem. (1965) 4, 804.

150. C.C.Addison and D.F.Sulton - Prog. Inorg. Chem. 1967) 8,1169.

151. B.M.Gatehouse, S.E.Livingstone and R.S.Nyholm - J. Chem. Soc. (1957) 4227.

152. Addison C.C. & Gatehouse B.M. Chemy. Ind. (1958) 4641.

153. Greenwood N.N-J. Chem. Soc. (1959) 3811: M.S.Ram and J. Hupp- Inorg. Chem. 30 (1991) P 130.

154. Caira M.R.Haigh J.M.AND Mesimbeni L.R.J. Inorg. Nucl. Chem. 34 (1972) 3171. F.corazza carlo Floriani and A.C.Villa Inorg. Chem. 30 (1991) 145.

155. Bereman R.D. & Nalewaje K-J. Inorg. nucl. Chem.40 (1978) 1313.

156. Biradar N.S.& Locker A.L. J. Inorg. nucl. Chem. 37 (1975) 1308. Pfeiffer P.& Pfitzner H.J.Prakt. Chem 145 (1936) 243.

157.   Hasty E.F.Wilson,L.J.& Hendrickson D.N.Inorg.   Chem.   17
        (1978) 2908.

158.   Peyronel   G.Gebretti   A.C.& Pellacani G.C.J.Inorg. Nucl.
        Chem.35 (1973) 973.

159.   Nakamoto K.Infrared Spectra of Inorganic and Coordination
        compound willy N.Y. (1970).

160.   Biradar N.S.& Locker A.L.J.Inorg.   Nucl.   Chem.37 (1975)
        1308.

        pfeiffer P.& pfitzner H.J.Prakt Chem.145 (1936).243.

161.   Hasty   E.F.Wilson L.J.& Hendrickson   D.N.Inorg.   Chem.17
        (1978) 2908.   A.Mcauley,   and S.Subramaniam- Inorg. Chem.
        vol. 30 (1991) P 371.

162.   Singh D.P.Chauhan,   V.K.Rana,   V.B.& Teotia M.P.J.Coord.
        Chem.13(1984) 159.

163.   Green wood. N.N.& Wade K.J.Chem.Soc. (1960).13(1984) 159

164.   K.Giridhara Reddy,   K.   Hussain Reddy & D.Venkta   Reddy-
        Indian J. Chem. Vol. 25A (1986) pp. 982-984.

165.   Nnakamoto   K-nfrared Spectra of inoganic and coosdination
        compounds (John Willy New York) 1970.

166.   Jain M.C.Srivastava A.K.& Jain P.C.Inorg.   Chem. Acta 23
        (1977) 199.

167.   Strtes J.G.MC carthy C.H.& quill L.L.J.Am. Chem. Soc. 71
        (1948) 3142.   M.P.Suh, S.G.Kang. V.L.Goedklu and S.H.Park
        - Inorg. Chem.30 (1991) P-365.

CHAPTER-II

PHYSICAL MEASUREMENTS AND METHODS OF CALCULATION

PHYSICAL MEASUREMENTS

(a) Magnetic Me-asurements

The magnetic susceptibility of the isolated complexes were measured in powder form using GUOY'S balance. Mercury (II) tetrathiocyanato cobaltate (II) [HgCo (CNS)4] (Xg = 16.442 x 10 CGS units at 293 A) was used as calibrant. Tube constant was calculated from time to time to check the satisfactory working of the apparatus. The measurements were carried out in the Department of Chemistry, Delhi University, Delhi; and University of Roorkee, Roorkee.

(b) Infrared Spectral Studies - Infra red spectra of the compounds were recorded on a Perkin-Elmer 621 spectrophotometer in KBr pellets. These measurements were carried out at Indian Grass Land research Institute Jhansi.

(c) Electronic Spectral Measurements- The electronic /Reflectance spectra of the complexes were measured in non aqueous media using Bausch and Lomb spectronic 20 and Perkin Elmer-621 Spectrophotometer at room temperature.

(d) pH-Measurements- pH- measurements were made at room temperature on an Elico pH-meter-using glass electrodes.

(e) Chemical Analysis- The metal complexes in all the complexes were estimated as follows.

A known weight of the complex was decomposed with a mixture of conc. HNO3 and H2SO4 by heating. The organic matter was filtered and the residue was dissolved in doubly distilled water or some times dilute hydrochloric acid was added to it and made upto a known volume, from which the metal contents were estimated by standard literature methods. The micro analysis of carbon, hydrogen and nitrogen for the ligands and the isolated complexes was done at Modi Steels, Modinagar and Modi Rubber Ltd., Modipuram (Meerut).

Ligand Field Parameters

The various ligand field parameters such $Dqxy, Dqz, Dq$, Ds, Dt, Angular overlap parameters such as $d\sigma, d\pi, e'\sigma xy, e'\pi xy$, $e'\pi z, e'z$ and normalised spherical parameters e.g. DS, DT, DQ, DQxy and DQz have been calculated by the literature methods.[1-4]

Magnetism

Magnetic susceptibility (using GUOY'S balance) has been calculated using the formula

β = 16.44 x 10-6 x Room temperature k x w/ Temp. k, Δw's

Δ w's = (Δ ws - δw)

δw = the change in the weight of the empty tube.

Δs = the change in weight of the calibrant.

w = weight of the calibrant

Xg = β x Δw'T/ w

Xg = gram susceptibility of the complex

β = tube constant

w   = weight of the complex

$\triangle$w'T = change in the weight of the complex

μeff = 2.828 $\sqrt{}$ XM' x 10-6   x T

μeff = magnetic measurement at temperature (T).

XM' = Molar susceptibility corrected for dimagnetism

(according to the values suggested by Figgis and Lewis).

T - absolute temperature.

The magnetic susceptibility measurements 5 were carried out by the GUOY method using a thin pyrex glass tube (1.2 cm an internal diameter and 15 cm long). The calibration of the balance was done by using conductivity water and this water was also used as reference solvent. All susceptibility measurements were carried out at room temperature.

Covalency Factor or Nephelauxetic Ratio-

Covalency factor (β) has been calculated by using the relation β = B (in complex)/B (in Freeion). The value of β = 1.0 indicate 100% ionic character while β = 0.5 indicates 100% covalent characte. Thus the values β- between 0.5 and 1.0 clearly suggests the partial covalency character.

Ligand Field Splitting Energy (10Dq or $\triangle$)

It is the orbital separation energy between γ5 or t2g and γ3 or (eg) often represented by 10 Dq or $\triangle$. In all the systems 10 Dq has been calculated using the equations suggested by Figgis 6 and Ballausen 7 .

Racah's Inter-Electronic Repulsion Parameter

Where the interaction between two or more electrons are involved, it is possible to write down the energy for each term above the ground term, which arises as an expression involving several parameters. The energies are a function of the electron repulsion parameters. The two parameters can be chosen either the condon shortly8 parameters (F0, F2, F4) or · the Racah's interelectronic repulsion parameters (A, B, C)9,10. These parameters are sufficient if attention is restricted to d-electrons. If for example, f-electrons are considered other parameters are sufficient if attention is restricted to d-electorn. If for example, f-electrons are considered other parameters to extend the set must be incorporated. Excitation energies of some multiple terms in spherical symmetry expressed in Racah parameters (B) and (C) of interelectronic repulsions are given below in table No.2 and 3.

TABLE - 1

CONDUCTANCE (Ohm^{-1} cm^{-2} mole^{-2}) DATA OF ELECTROLYTIC COORDINATION COMPOUNDS

Electolytic Nature	Concentration	Nitro-methane	Acetone	Aceto-nitrile	DMF	Methanol	Ethanol	DMSO
1:1	10^{-3} M	20-30	120	120-160*	65-90	80-115	35-45	50-60
	10^{-4} M	-	135	-	-	-	-	-
2:1	10^{-3} M	50-60	180	220-300	130-170	160-220	70-90	-
	10^{-4} M	-	320	-	-	-	-	-
3:1	10^{-3} M	70-82	-	340-420	200-240	~330	121,330**	~110
	10^{-4} M	-	446	-	-	-	-	-
4:1	10^{-3} M	90-100	-	-	-	-	-	-

(Solvents)

* Walton, R.A., Quart. Rev., 19,126 (1965).

** J.H. Hickfort and J.E. Ferguson -J. Chem. Soc.(A), 1048, (1968).

Table No.2- Relevant excitation energies of some of the terms for d^n configurations are given below:

TABLE 2

Ground term	d5	Ground term	3d3 & d7	Ground term	d2 & d8
6S	0	4F	0	3F	0
4G	10B+5C	2G	4B+3C	1D	5B+2C
4P	7B+7C	4P	15B	3P	15B
4D	17B+5C	2P	9B+3C	1G	12B+2C
4F	22B+7C	2H	9B+3C	1S	22B+7C

Table No. 3- Free ion values of B and C for different gaseous11-
12 ions based on electronic configuration:

TABLE 3

Electronic configuration	ion	B	C
3d2	V+3	816	4165
3d3	Cr+3	918	3850
3d4	Mn+3	1140	3675
3d5	Mn+2	960	3525
3d6	Fe+2	1058	3901
	Co+3	1100	----
3d7	Co+2	971	4366
3d8	Ni+2	1041	4831
4d6	Rh+3	720	----
4d8	Pd+2	683	2620
5d4	Os+4	700	----
5d6	Ir+3	600	----
	Pt+4	720	----
5d8	Pt+2	600	

Ligand Field Stabilisation Energy-

Ligand field stabilisation energy is simply given by the
energy gain in units of Dq for the ground state. Following table
represents the value of L.F.S.E. for different electronic
configurations. Actually L.F.S.E. is known as the difference
between the lowest energy level of a term split by a ligand field
and the centre of gravity of the term in the ligand field.

L.F.S.E. Values for different electronic configurations

TABLE 4

Electronic Configuration	L.F.S.E. for octahedral complexes	
	Weak Field	Strong Field
d1	4Dq	4 Dq
d2	6Dq	8Dq $-(3F2 - 15F4)$
d3	12Dq	12 Dq
d4	6DQ	16Dq $-(6F2 + 145F4)$
d5	0Dq	20Dq $-(15F2 + 275F4)$
d6	4Dq	24Dq $-(5F2 + 255F4)$
d7	6Dq	18Dq $-(7F2 + 105F4)$
d8	12Dq	12 Dq
d9	6Dq	6 Dq

L.F.S.E. = X.Dq/350 (X-varies according to d^{n_i} configuration)

Spin Orbit Coupling Constant (λ)

The spin orbit coupling constant of the ions where complete quenching is expected has been calculated using the formula

$$\mu = \mu_0 (1 - \alpha\lambda / 10 \, Dq)$$

where μ - observed magnetic moment in B.M.

μ_0 - spin only moment in B.M.

α - A constant (4 for F-ground state ion and 2- Dq for D-ground state ion).

10 Dq - Ligand field splitting energy.

Lande's Splitting Factor (g) in Octahedral Fields

The value of Lande's splitting factor has been calcul
by the given formula

$$g = (2 - 8 \lambda / 10 Dq)$$

where λ - spin orbit coupling constant

10 Dq - Ligand field splitting energy

Preparation of Copper Bromide- Copper bromide was prepared by

meta thesis procedure i.e. by mixing 3.40 gm of cucl2 and 2.4
of KBr in absolute ethanolic medium. Potassium chloride
removed by filtration and the filtrate containing copper bro:
was used for the preparation of the complex 13.

Copper Iodide

It was prepared by mixing (10 m mole) of the CuCl2
20 m mole of potassium iodide in the same solvent (abso
ethanol). Potassium chloride was removed by filteration and
filterate containing copper iodide was used for the com
formation.

Copper Thiocyanate

It was prepared from potassium thiocyanate and cop
chloride in absolute ethanol.

Manganese chloride and bromide were obtained by mix
the calculated amount of lithium chloride and bromide in the
acetate complex.

1.)<u>Analytical</u> <u>Measurements</u>

The cobalt (II) and nickel (II) and other metals   cont

in the complexes were   estimated(14)   by EDTA   titrimetry   us

Erichrome Black-T as an indicator and copper (II) content in

complexes   was   estimated Iodometrically' following   stand

literature method (15) After destroying the organic residues f

with   aqua   regia   and then   with   concentrated Sulphuric   ac

Halides were   estimated   by Volhard's method   and   nitrate

determined   as   is   nitrone   salt.   The   thiocyanate   (SCN)

Selenocyanate (SECN)ions were estimated as silver thiocyanate

Selenium metal respectively.

2.)<u>Physico-Chemical</u> <u>Measurements</u>

Conductance measurements were done by Elico   conductivi

bridge at a concentration level of 10-3 M based on formula wei

of the analysed complex.

1.   J.C.Donini,B.R.Hollebone   The   Derivation   and
        and A.B.P.Lever   Application   of Spjeric
                                      Harmonic Hamiltoniahns
                                      by S.J.Lippard in Progre
                                      in Inorganic Chemistry
                                      vol.22,(John   Willey   a
                                      sons Inc. ,p.225,(1975).

2.   J.C.Donini, B.R.Hollebone, Inorg. Chem., 14,455,(1975)
        G.London, A.B.P.Lever and J.C.Hempel

3.   A.B.P.Lever   Coord.   Chem.   Rev; 3, 11

                                      (1968).

4.   A.B.P.Lever   Inorganic   Electronic

                                      Spectroscopy-Amsterdam

                                      Elsevier-1968.

5.   B.N.Figgis   and J.Lewis in " Modern   Coordinatio
chemistry" J.Lewis and R.G.Wilkins- Eds.Inter Science, New York,
(1960), pp. 400-454.

6.   B.N.Figgis and J.Lewis   "Techniques of Inorgani
Chemistry" Interscience, N.Y.,Vol. 4, p.137 (1965).

7.   C.J.Ballhausen -" Introduction to Ligand Field Theory"-
McGraw Hill, New York, 1966.

8.   W.E.Hatefield and R.Whyman - Transtion metal Chemistry
Vol.V,7 (1969).

9.   B.N.Figgis " Introduction to Ligand Fields" - John Wille
& Sons. Inc. , N.Y.,pp.216 (A) pp.233-315(B), 1968.

10.   R.L.Carlin " Transition Metal Complexes", Marcoes Dekkar
N.Y. pp. 115-120, (1960).

11.   C.K.Jorgensen   Mol. Phys.,2,309,(1959).

12.   P.J.P.Williams   J.Chem. Soc. (A),137 (1955).

13.   S.K.Madan and H.H.Denk, J.Inorg.Nucl.Chem.,27,1273(1957)

14.   F.J.Welcher " The analytical used of EDTA" van Nostr an
New York. (1958).

15.   A.I.Vogel " A Text book of quan titative Inorgani
Analysos" Longmand ,London, (1961)

CHAPTER-III

Preparation and Characterisation of Ligands

(1) P-methoxy Benzyl Thiosemicarbazone

It was prepared by the reported literature method (1-2) by heating one mole of thiosemicarbazide in 300 ml. of water and 20 ml. of glacial acetic acid, a clear solution was obtained. To this one mole of p-methoxy benzaldehyde in ethanol was added. After refluxation for about two hours on concentration and cooling white long crystals were obtained. These were crystallised with ethanol, m.p. 170 C (C 9 H 11 N 3 OS).

(2) Phenyl glyoxal Thiosemicarbazone:-

Phenyl glyoxal was prepared by the oxidation of acetophenone with selenium dioxide as follows:-

In a 500 ml. three necked flask fitted with a liquid sealed stirrer a reflux condenser and a thermometer place 300 ml. of dioxane 55.5 g. of selenium dioxide and 10 ml. of water in the flask,heat the mixture to 50-55 0/C and stirrer until the solid has dissolved. Remove the thermometer momentarily and add 60 gm. of 2.5 dimethoxy acetophenone in one lot replace the thermometer. Reflux the mixture with stirring for four hours, after about two hours the solution becomes clear and little further precipitation of selenium is observable. Decant the hot solution from the precipitated selenium through a fluted filter paper and remove dioxane and water by distillation through a short column. Distil the residual2.5 dimethoxy phenyl glyoxal under reduced pressure from a 150 ml. claisen flask and collect the fraction boiling at 95-97 0/C/25mm. The yield of pure 2.5 dimethoxy phenyl glyoxal

(yellow liquid) is 48 g. this sets to a stiff gel on standing, Probably as a result of polymerisation, but may be recovered without appreciable loss by distillation.

The aldehyde is best preserved in the form of the hydrate, which is prepared by dissolving the yellow liquid in 3.5 - 4 volumes of hot water and allowing to crystallise 2:5 Dimethoxy phenyl glyoxal hydrate also crystallises from chloroform, alcohol (Rectified spirit) upon distillation under diminished pressure the free aldehyde is obtained. Glyoxal thiosemicarbazone is prepared by the method given in Vogel (Loc. Cit).

(3)   4-p-methoxy phenyl thiosemicarbazone of 2:5 Dimethoxy phenyl glyoxal:-

The Schiff base was synthesised by refluxing p-methoxy Benzyl thiosemicarbazone with 2:5 Dimethoxy phenyl glyoxal in ethanol in 1:1 ratio in the presence of anhydrous sodium acetate and few drops of glacial acetic acid for 3-4 hours. The reaction mixture after concentration and cooling gave the Brown colour mass, which was crystallised with alcohol m.p. 178 C ($C_{19}H_{19}N_3O_4S$).

(4)   2-amino-5-chloro Benzophenone was procured from Wilson Lab (U.S.A.).

(5)   N-methyl-S-Benzyl dithio carbazate-

It was prepared according to a method as described by Akbar Ali (4).

(6) α -N-methyl-S-Benzyl-β-N-2:5 Dimethoxy (phenyl glyoxal) methylenedithiocarbazate :- (C19 H20 N2 O3 S2) α-N-methyl-S-Benzyl-β-N-(Orthohydroxy 2:5 Dimethoxy phenyl glyoxal) methylenedithiocarbazate (C19 H2o N2O3 S2) and α-N-methyl-S-Benzyl-β-N(2-amino-5-chloro Benzophenone) methylene dithio carbazate (C22 H17 N3 S2 Cl) were prepared by following the reported methid (5). 4.0 gm 2:5 Dimethoxy phenyl glyoxal/2-amino-5-chloro-Benzophenone was added to a solution of N-CH3-S-benzyldithio carbazate (2.0 gm.) in 95% ethanol (20 ml).

The mixture was refluxed on steam bath for about half an hour, where wpon the yellowish white crystalline mass was formed. It was purified by acetone.

(7) (Salicylidene-O-amino) Benzophenone; (5-Methoxy salicylidene-O-amino) benzophenone; (5-Chloro salicylidene-O-amino) benzo phenone and (5-ethyl salicylidene-O-amino)-benzo-phenone. The abov3e Schiff bases were prepared by appropriate condensation of aldehydes(6) with O-amino benzophenone by refluxing in ethanol or by heating at 180 without any solvent followed by recrystallisation from Petroleum ether-acetone. Purity of these anils were checked by TLC, and characterised by elemental analysis and IR frequencies.

I.R. Studies:- Spectrophotometer show that a compound absorb certain frequencies of radiation, when radiant energy is absorbed by a compound. Some feature of structure in the molecule is altered in a small but very specific way. Each frequency of radiant energy that a molecule absorbs correlates with some

particular unit of structure. The IR spectrum does not tell us, is the total size of the molecule and number of groups of each kind. Each IR absorption consists of a certain breadth of frequencies rather than exclusively one frequency and therefore, is referred to as an absorption band.

The infrared spectra of the various compounds are given in the tabular form. Some important frequencies are discussed.

The absorption bands at 1380 cm -1 and 1460 cm -1 represent (C-H) bending vibrations. The overlaping bands in the region 2850 to 2980 cm -1 are all due to (C-H) stretching, not only are there symmetric and asymmetric stretchings, but the CH3,-CH2 and CH groups each have slightly different frequencies.

The (C-C) skeletal vibrations that might be expected are very weak and for unbranched alkanes are barely visible. In the spectrum three bands characteristics of alkyl (C-H) vibrations at 2900, 1460 and 1380 cm -1. Additionally there is an intense, broad band at 3350 cm -1 due to (O-H) stretching and a strong, rather broad band near 1100 cm -1 caused by (C-O) stretching.

1.   Vibration due to >C=O and -CH=N group:-

Ketonic and azomethine frequencies are appeared at around (1680-1700 cm -1) and (1620-1640 cm-1) respectiveky (7-8), as medium strong bands, (C-H) bonding modes of Benzene are observed as medium to medium sharp bands in the region (1400-1470 cm -1), while (C-H) in plane deformations are obserable in the region 1230-1280 cm -1.

2.   <u>Vibrations due to mercapto (thiourea moiety)</u>-

The bands observed in the region 1300-1370 cm -1 are tentatively assigned (9) to [ν(C=S) + ν(CN)]. For ν(C=S) different regions ~1400 cm -1 and ~730 cm -1 have been prefered by Irving etal(10) and Stewart(11), while the region 1000 cm -1 Yamagauchi(12). In the present cases bands around 810 cm -1 (>C=S) along with some overlap in the region (1300-1370 cm -1) due to ν(C=S) + ν(CN) have been noticed.

3.   <u>Vibration due to phenolic (OH)</u>- The medium band observed at 1270 cm -1 and 3500 cm -1 in the spectra of some ligands is ascribed due to the phenolic (-C-O) and (OH) stretching vibrations(13). In some cases broad and weak band in the region 2700-2930 cm -1 is also observed and is assigned to intramolecular H-bonded OH(14-15) group between hydroxyl hydrogen and nitrogen of azomethine group forming a stable six membered ring(16-18).

TABLE-3.1

Chemical Analysis Data of Schiff Bases.

S.No.	Compound	M.P. oC	Colour	% Calcd (Found) C	H	N	S/Cl
1	(C9 H11 N3 OS)	170	White	51.67 (50.78)	5.26 (5.00)	20.09 (19.85)	15.31 (14.83)
2	C11 H13 N3 O3S	173	White	49.43 (49.0)	4.86 (4.75)	15.73 (15.10)	11.98 (11.71)
3	(C19 H19 N3 O4S)	181	Brown	59.22 (58.12)	4.93 (4.10)	10.90 (9.64)	8.31 (7.58)
4	(C19 H20 N2 O3S2)	140	Brown	58.76 (58.00)	5.15 (4.95)	7.21 (7.12)	16.49 (16.31)
5	(C18 H16 N2 O4S2)	165	Brown	55.67 (54.26)	4.12 (4.85)	7.21 (7.10)	16.49 (16.20)
6	(C22 H21 N3 S2)	173	Brown	67.51 (66.31)	5.37 (5.67)	10.74 (9.89)	16.36 (15.98)
7	(C21 H17 NO3)	125	Brown	76.13 (75.15)	5.13 (4.60)	4.22 (4.10)	–
8	(C22 H19 NO2)	137	Reddish Brown	71.53 (69.99)	5.77 (5.00)	4.25 (4.18)	–
9	(C20 H14 NO2 Cl)	104	Brown	71.53 (75.10)	4.17 (4.08)	4.17 (3.98)	10.58 (9.72)
10	(C22 H19 NO3)	146	Brown	76.52 (75.34)	5.50 (4.68)	4.05 (3.96)	–

TABLE--3.2

Important IR Frequencies of Schiff Bases

S.No.	Compound	NH Stretch	ν_{OH}	$\nu_{(C=N)}$ AND NH-Bending in Plane	CH-benzene in Plane	$\nu_{(C=S)+}$ $\nu_{(CN)}$	$\nu_{C=O}$	$\nu_{(C=S)}$ Thiourea	$\nu_{(NH)}$ out of plane
1	(C9 H11 N3 OS)	3340(s) 3270(vs) 3180(ms)	-	1640 (m)	1410(m) 1460(m)	1300(vs) 1370(s)	-	810(s) 1215(m)	670(m)
2	(C11 H13 N3 O3S)	3400(ms) 3290(m) 3290(m)	-	1635(m)	1440(m) 1450(m)	1350(vs)	1690(s)	805(s) 1220(m)	680(m)
3	(C19 H19 N3 O4S)	3350(m) 3400(ms) 3210(m)	-	1635(m)	1440(m) 1450(m)	1360(vs)	1700(s)	810(s) 1220(m)	670(m)
4	(C19 H20 N2O3S2)	-	-	1640 (m)	1440(m) 1460(m)	1300(s) 1350(vs)	1680(s)	805(s) 1220(m)	-
5	(C18 H16 N2O4 S2)	-	2840(m) 3540(m)	1640 (m)	1440(m) 1400(m)	1350(vs) 1300(s)	1700(s)	800(s) 1220(m)	-
6	(C22 H21 N3S2)	-	-	1640 (m)	1400(m) 1440(m)	1360(s) 1310(s)	-	810(s) 1220(m)	-
7	(C21 H17 NO3)	-	2950(m) 3100(m)	1630(m)	1410(m) 1470(m)	-	1690(s)	-	-
8	(C22 H19 NO2)	-	2900(m) 3000(m)	1630(m)	1400(m) 1470(m)	-	1700(s)	-	-
9	(C20 H14 NO2 Cl)	-	2830(m) 3100(m)	1630(m)	1400(m) 1470(m)	-	1700(s)	-	-
10	(C22 H19 NO3)	-	2900(m) 3030(m)	1625(m)	1400(m) 1470(m)	-	1700(s)	-	-

m= medium   ms- medium sharp   mb= medium broad
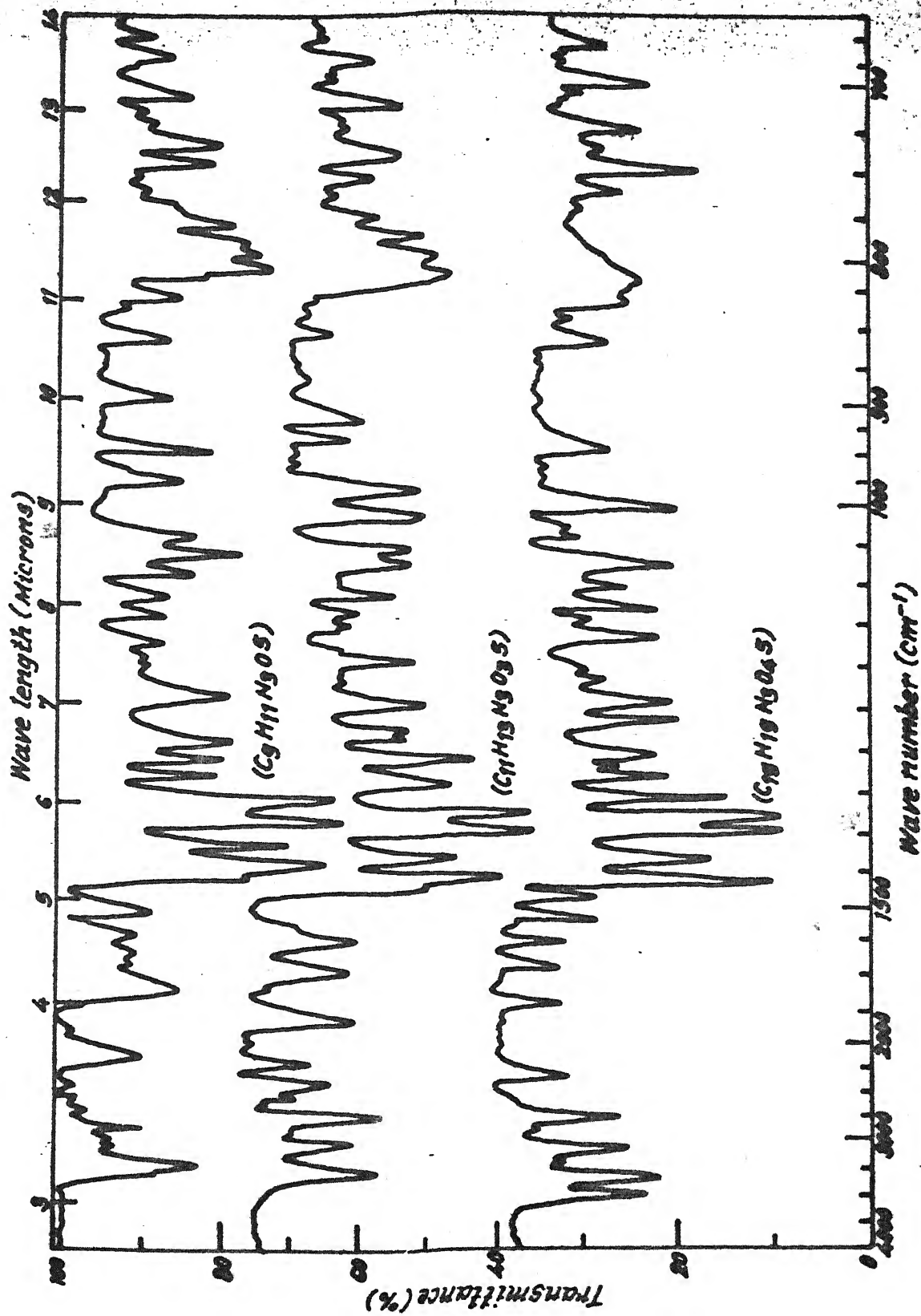
Fig.(3.1) : I.R. Spectra of organic compounds.
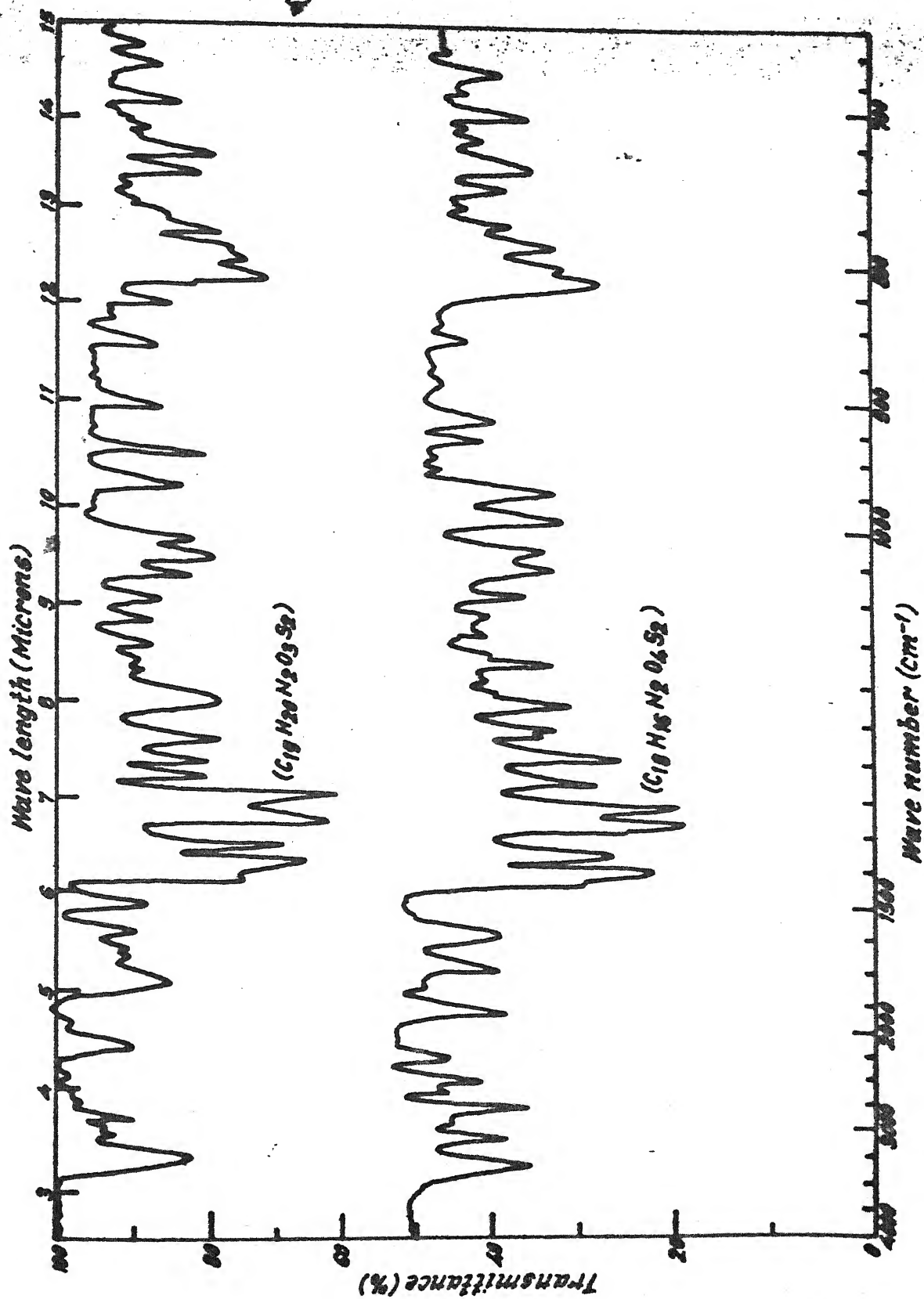
Fig.(3.2): I.R. Spectra of organic compounds.
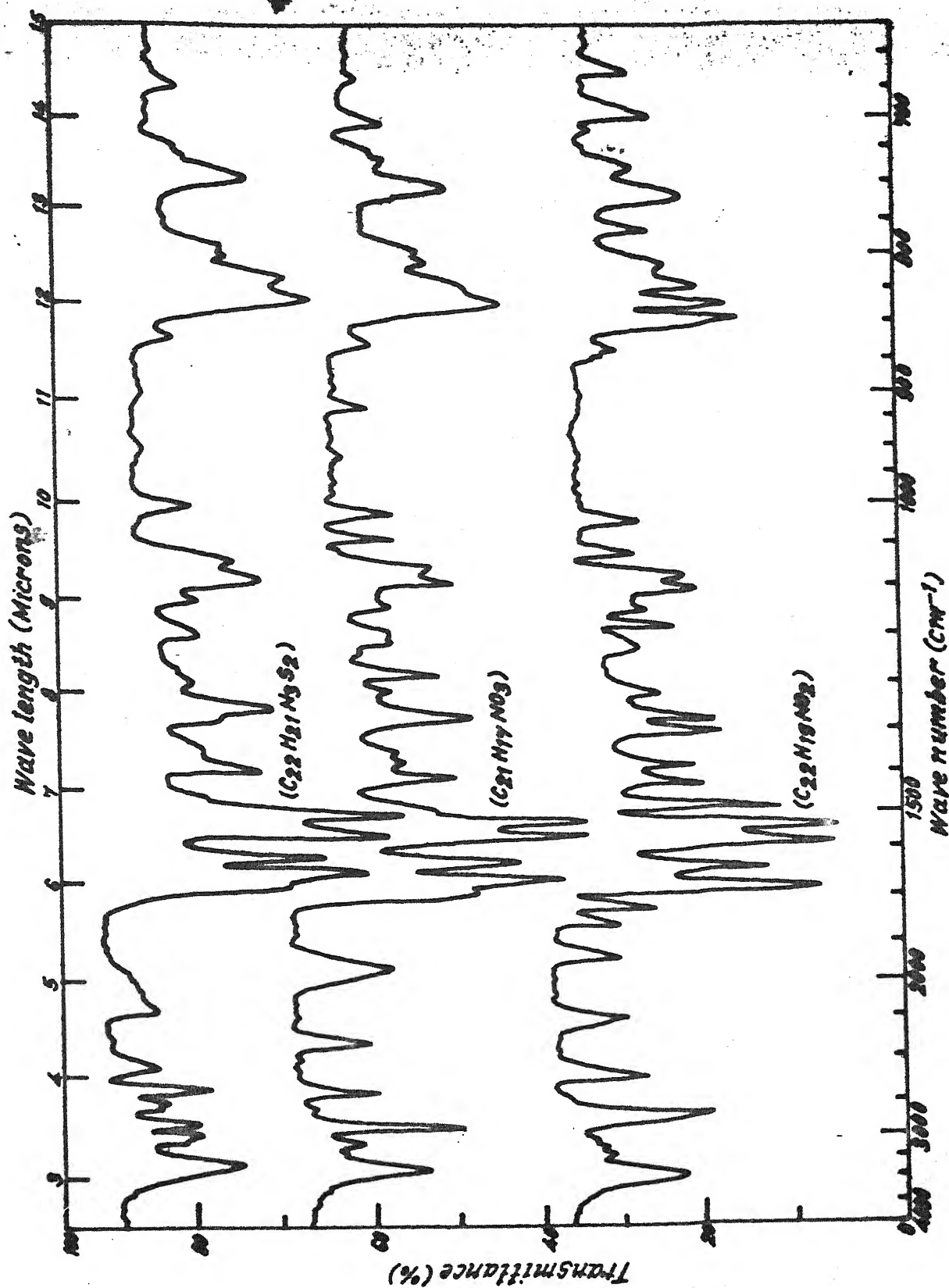
Fig.(3.3): I.R. Spectra of organic compounds.
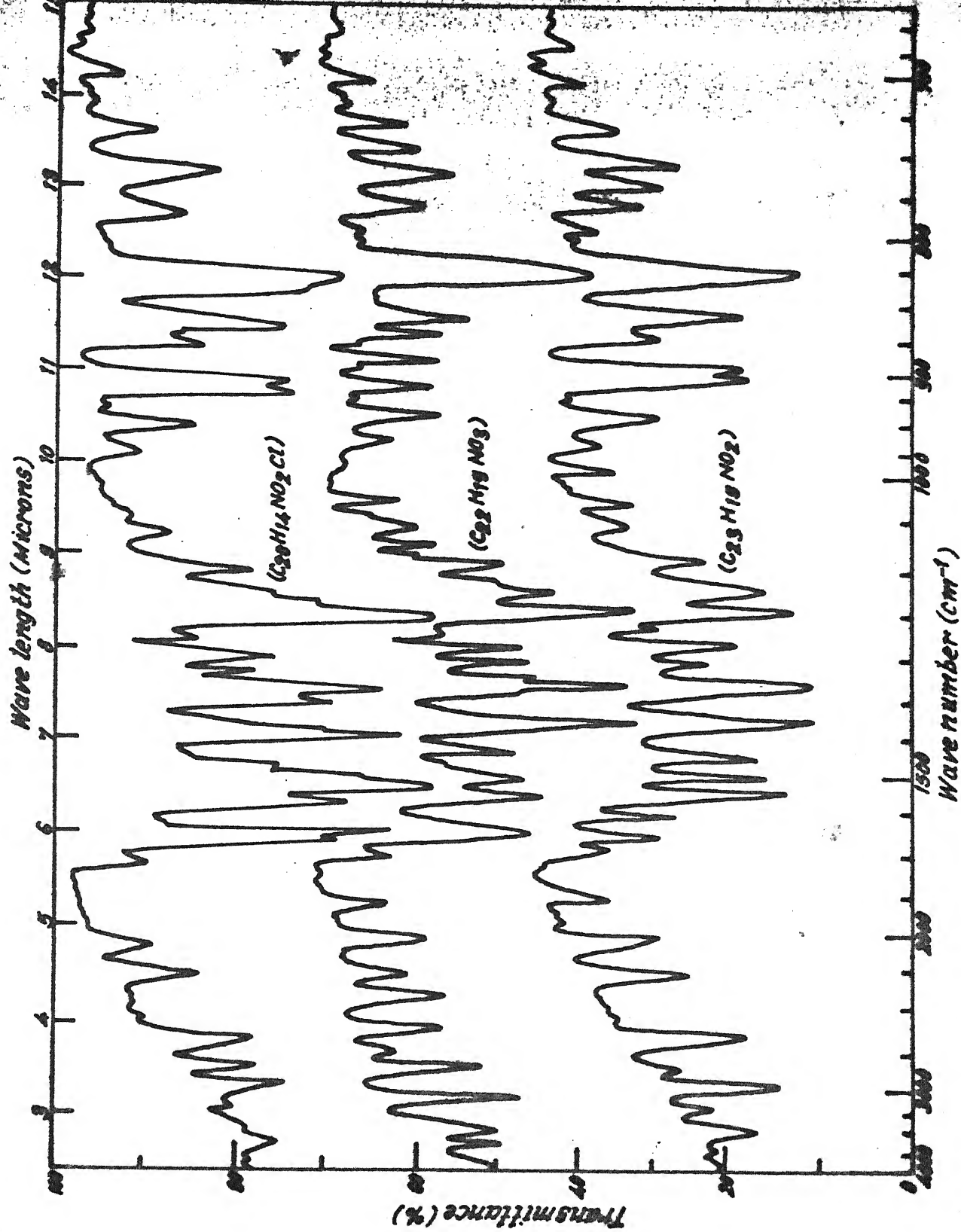
Fig.(3.4): I. R. Spectra of organic compounds.

CHAPTER - III

REFERENCES

1. G.N. Mukherjee and P. Dhar - J. Ind. Chem. Soc. (1980), 57, 241.

2. R.S. Verma - Jour. Ind. Chem. Soc. (1966), 43. 558/

3. Arthur.I.Vogel -"A Text book of practical organic chemistry"- Third edition Longman group Limited, p.866.

4. M. Akbar Ali and S.G. Teoh - Jour. Inorg. Nucl. Chem. 40, 451 (1978).

5. M. Akbar Ali et. al - Jour. Inorg. Nucl. Che. 6, 41(1980); 890(1979).

6. J.L. Norula, Sudagarmal and M.S.M. Rawat - Jour. Ind. Chem. Soc. 63, 652 (1981).

7. J.E. Kovacic - Spectrochim Acta Pt A (1967), 23, 183.

8. P.Teyssie and J.J. Charette - Spectro Chim. Acta. (1963), 19, 1407.

9. B.C. Saha, R.P. Bhatnagar and S.K. Banerjee - Ind. J. Chem. 59 (1982) 927.

10. HMNH Irvin and K. Swaminathan - Jour. Inorg. Nucl. Chem. 26 (1964) 1291.

11. J.E. Stewart - Jour. Chem. Phys. 26 (1957) 248.

12. A. Yamagauchi, R.B. Penland, S. Muzuchima, T.J. Lane and C. Curran - Jour. Am. Chem. Soc. 80 (1958) 527.

13. R.M. Silverstein and G.C. Bassler - Spectrometric Identification of Organic compounds "John Wiley New York (1963).

14.   N.B. Colthup, L.H. Daly and S.E. Wiberley -"Introduction to infrared and Raman spectroscopy" Academic press New York (1963).

15.   J.R. Dyer "Applications of absorption spectroscopy of organic compounds" Prentice Hall, London (1974).

16.   Harland. D. Embree - Brief Course organic chemistry - Scott Foresman and company, GleN.view Illinois.

17.   Y.D. Kulkarni, Nishi Saxena and O.P. Srivastava - Ind. Jour. of Chem. 29 A (1990) 77.

18.   J.P. Collman and L.S. Hegedus - principles and applications of organotransition metal chemistry (Science Books) chapter 14, 1980.

CHAPTER - IV

Structural Studies on high spin octahedral Iron(III) complexes with Schiff bases derived from substituted salicylaldehyde and O-amino benzophenone.

Introduction:- The chelating properties of Schiff bases containing ONS donor sequence are well established. These compound possess analytical as well as biological activities. Metal hexacyano-ferrates (II) used as inorganic ion exchangers (1-2). In column (3) and paper chromatography of metal ions. Ferrous chloride required was prepared by Mellor method(4). Recent trend in the chemistry of coordination compounds has been the search for complexes containing multi metal centres(5-8) and their sereening as models of bio. inorganic molecules. Fe(III) complexes of unsaturated Schiff base are having intense dark red colour. This colour is usually ascribed to the presence of one or more low lying charge transfer bands. Because these very intense (d-d) transitions in the visible spectra of such compounds could not be observed. Positions and intensities of these bands are slightly sensitive to the anions. The electronic spectra offer evidence for micro geometry around the central and complexed Fe (III) derivative.

In multidentate chelating agent all donor atoms cannot be of equal size and strength therefore- in such an environment, the possibility of obtaining the complexes of idealised symmetry appears to be remote and the presence of the elements of lower symmetry or distortion seems to be a reasonable feature.

Distortion plays an important role in biological and Industrial systems. Several-N-substituted salicyldimine (Sal-NR) complexes(9) of the general formula [Fe (Sal-NR)2 X] (where X=Cl, Br, CH3COO) have been found to show normal high spin behaviour by obeying Curie-Weiss Law(10-12). In contrast, the related [(Fe Salen X)] derivatives showed reduced magnetic (13) moment (~5.2 B.M.). These complexes have been found to be dimeric in the solid state with approximately square pyramidal geometry around each iron atom (14). The lowering of magnetic moment is due to weak antiferromagnetic interactions. Recently, Taylor and Patton(15) have reported several iron(III) complexes with pentadentate ligands involving nitrogen, oxygen and sulphur magnetophores, with normal magnetic behaviour. Several square pyramidal Iron (III) complexes with an intermediate spin systems of temperature independent magnetic moments of about 3.9 B.M. have recently been reported (16-17).

In this chapter we have reported analytical, magnetic Infrared and electronic spectral properties of Fe(III) complexes with 5-methoxy Salicylidene-O-amino-benzophenone, 5-ethyl-Salicylidene-O-amino benzophenone, 5-chloro-salicylidene-O-amino benzo-phenone and 5-ethoxy salicylidene-O-amino-benzophenone.

EXPERIMENTAL:

A Brownish red coloured complex was obtained by adding (0.805 g, 0.005 M) of anhydrous FeCl3 and different substituted

salicylidene-O-amino benzophenone (0.01 M) in ethanol. The pH-was reised to 6-6.5 by alcoholic ammonia. The whole content was refluxed for two-three hours. The content on concentration to half of its volume, and on subsequent cooling gave brown coloured precipitate. It was filtered washed with alcohol and dried completely in hot air oven (temp. 110 C). In the complex Iron was estimated by using 1:10 - phenanthroline / EDTA complexometric titration.

RESULTS AND DISCUSSION:

Magnetic Studies:- Five and six coordinate complexes possess either D3h (trigonal bipyramidal or square pyramidal geometry with C4V symmetry. In two idealised symmetries, metal ions can assume either a low- or high- spin configuration according to whether the energy separation between the two highest orbitals in each.

Table (4.1) Analytical and magnetic date of Iron (III) Complexes.

S.No.	Compound	% calcd/ (Found)				$X_1 mx -6$ 10 Cgs Unit	μ_{eff} (B.M)	Stereo chemistry
		C	H	N	Metal			
1	[Fe (C 21 H16 NO3)2] cl.H2O	65.02 (65.50)	3.95 (4.15)	3.48 (3.63)	7.01 (7.25)	14022.54	5.82	H.S.O.
2	[Fe (C 22 H18 NO2)2] cl	73.85 (74.17)	4.98 (5.05)	3.78 (3.93)	7.60 (7.84)	13427.61	5.66	H.S.O.
3	[Fe (C 20 H13 NO2 cl] cl	62.84 (63.12)	3.13 (3.41)	3.20 (3.68)	7.19 (7.34)	17903.82	5.84	H.S.O.
4	[Fe (C 22 H18 N2O3)2] cl	67.08 (67.74)	4.07 (4.61)	3.15 (3.59)	7.04 (7.16)	14052.47	5.8	H.S.O.
5	[Fe (C 21 H16 NO3)2] (NH3)	67.87 (68.77)	4.12 (4.77)	5.26 (5.73)	7.02 (7.62)	14638.84	5.91	H.S.O.
6	[Fe (C 22 H18 NO3)2] 2NH3	66.83 (67.87)	5.02 (5.39)	6.98 (7.19)	6.88 (7.18)	14001.2	5.78	H.S.O.

High spin orbit -- H.S.O

Table (4.2) Electronic spectral data and relevant ligand field parameters.

S.No.	Compound	Observed bands and their assignments (cm-1)		10 Dg cm-1	B cm-1	C cm-1	β_{35}
1	[Fe (C21 H16 NO3)2]Cl H2O	13130	6 Alg---> 4 T1g (G)	13130	1190	4763	0.9132
		16220	6 Alg---> 4 T2g (G)				
		24050	t2g --->π eg x				
		28900	π --->				
		36400	π ---> π x				
2	[Fe (C22 H18 NO2)2]Cl	13215	6 Alg---> 4 T1g (G)	13215	1200	4800	0.9209
		16470	6 Alg---> 4 T2g (G)				
		24000	t2g --->π eg x				
		27980	π ---> x				
		36600	π ---> π x				
3	[Fe (C20 H13 NO2 cl)2]Cl	12860	6 Alg---> 4 T1g (G)	12860	1169	4676	0.8971
		18760	6 Alg---> 4 T2g (G)				
		23200	t2g --->π eg x				
		27200	π ---> x				
		36100	π ---> π x				

Table (4.3) Electronic spectral data and relevant ligand field parameters.

S.No.	Compound	Observed bands and their assignments (cm-1)	10 Dg cm-1	B cm-1	C cm-1	β 35
4	[Fe (C22 H18 N2O3)2]Cl	14140 6 A1g ---> 4 T1g (G) 18720 6 A1g ---> 4 T2g (G) 24710 t2g --->eg 30105 41310	14140	1276	5104	0.9792
5	[Fe (C21 H16 NO3)2](NH3)	14100 6 A1g ---> 4 T1g (G) 18840 6 A1g ---> 4 T2g (G) 24700 t2g --->eg 30310 41500	14100	1281	4124	0.9831
6	[Fe (C22 H18 NO3)2]. 2NH3	13980 6 A1g ---> 4 T1g (G) 19300 6 A1g ---> 4 T2g (G) 24600 t2g --->eg 31500 40880	13980	1270	5080	0.9746

Table (4.4) Relevant ligand field Energy parameters in high spin Octahedral Iron Complexes

S.No.	Complex Compound	Δ k.k	F2 k.k	F4 k.k	(π-->t2g) k.k	eg-->π k.k	π→π	Y
1	[(Fe (C21 H16 NO3)2] cl. H2O	13.13	91.7	60.11	(15-80)	10.95	39.85	111.59
2	[(Fe (C22 H18 NO2)2] cl	13.2	92.47	60.61	(14.78)	10.8	38.78	287.7
3	[(Fe (C20 H13 NO2 cl)2] cl	12.86	90.08	59.05	14.34	10.34	37.54	70.07
4	[(Fe (C22 H18 N1 O3)2] cl	14.14	98.32	64.45	16.06	10.67	40.77	140.25
5	[(Fe (C21 H16 NO3)2](NH3)	14.1	105.03	64.7	16.21	10.6	40.91	12.8
6	[(Fe (C22 H18 NO3)2].2NH3	13.98	104.09	64.15	17.53	10.63	42.13	152.24

symmetry is higher or lower than the spin pairing energy. Experimentally it is found that "Soft" donor atoms such as asrsenic and phosphorous give rise low spin complexes. High spin complexes areobtained with ligands containing 'hard' donor atoms such as nitrogen and oxygen, while donor atoms such as sulphur Selenium halogen, thiocyanate, which occupy an intemediate position are capable of forming both high and low spin complexes(18-19). The spin state of paramagnetic ions is dependent upon the nature of the donors present in the ligand. Sacconi has given a comprehensive list of chromophores and predicted the spin state of various paramagnetic ions. Some exception are found in five coordinated complexeds(20). High spin octahedral complexes possess magnetic moment value close to 5.9 B.M. because the ground state has no orbital angular moment (21-22). The magnetic moment of the complexes under study are in the range 5.68-5.93 B.M., showing their high spin outer orbital octahedral stereochemical behaviour.

Electronic Spectral Studies:- Reflectance spectra were recorded using Mgo as reference. The spectra of all the complexes are identical in nature, showing similarity in their structures. Some of the bands are of low intensity and band beyond 25000 cm -1 may be presumably due to charge transfer. Electronic spectra differentiate between the various geometries possible for four and six coordinate complexes of d electronic configurations with the exception of d0 and d10 systems. The five coordinate species have distinct electronic spectra but it is generally difficult to

differentiate between square pyramidal and trigonal bipyramidal geometries due to the non rigid nature of such species (23,24). However the spectra recorded under the high pressure has proved of specific use in this direction (25).

The electronic spectra of high spin square pyramidal and trigonal bipyramidal, Iron(II) complexes involving pyridine based ligands have been reported by several workers (26-30). The electronic structures of five coordinate Iron(II) complexes with macrocyclic ligands resembling porphyrin derivatives (31->32), eg. deoxyhaemoglobin and deoxymyoglobin, shows three bands with maxima or shoulders in the region 5-20 KK along with two or three spin allowed transitions in D3h and C4V symmetries respectively(33). In the complexes of macrocyclic ligands, it is observed that the position of the low energy band depend upon the axial ligand field strength while higher energy band is primarily dependent upon the constant in plane macrocyclic ligand (34-35) field.

Recently, the electronic spectra of number of complexes of iron with quinquedentate ligands have been discussed(36,37). The brownish red colour Iron(III) complex shows one or more low lying charge transfer bands around 11000 cm -1 in the near Infra red region which has been assigned to ligand field transition(38). Iron(III) salts hydrolyses by water to gives yellow brown colour solution is not due to ligand field bands of Fe (H2O)6 + 3 but rather to charge transfer band (38).

Iron (III) complexes under study exhibits band in the region 12800-15000 cm -1; 16000-19800 cm -1; 23000-26000 cm -1; 27000-32000 cm -1 and 36000-42000 cm -1, which have been assigned to 6 A1g -> 4 T1 g(G) (d-d transition); 6 A1g -> 4 T2g (G) (d-d transition); t2g -> π * (charge transfer transition); π -> eg (charge transfer transition and π- π* respectively(39-41).

The transition 6 A1g -> 4 A1g gives directly the values of 10 Dq and B. Calculated values of B, C and B35 have been reported in tabular form using the following relationship.

$$\frac{6 \text{ A1g} -> 4 \text{ T1g}}{B} = 11.0 \text{ or } \frac{Dq}{B} = 1.10$$

C = 4 B and Fe +3 (B-Free ion) 1303. The value of charge transfer bands (π ---> t2g) and (eg --> π x) have been calculated using the following relations.

$$(\pi ---> eg) - \Delta = (\pi ---> t2g) \text{ in KK} \qquad (1)$$
$$(t2g ---> \pi x) - \Delta = (eg ---> \pi x) \text{ in KK} \qquad (2)$$
$$(\pi ---> t2g) + (t2g ---> eg) + (eg - \pi x) = (\pi ---> \pi x) \quad (3)$$

According to miller et.at (42) sum of (π --> t2g, (t2g -->eg) and (eg -->πx) in K.K. is equal to energy of the (π --> π x) transition for one electron molecular orbital. The value of (t2g --> eg) is equal to 10 Dq and can be evaluted by figgis equation.

$$\frac{6 \text{ A1G} ------> 4 \text{ T1G}}{B} = 24$$

The observed and calculated values for the transition ($\pi \longrightarrow \pi x$) are in the region 36 – 41 KK and 37 – 42 KK respectively, which are in good agreement for octahedral symmetry.

The values of λ and g are calculated (43) by the relationship.

$$\mu = \mu_0 \left(1 - \frac{\alpha \lambda}{10\ Dq}\right) . ; \quad g = \left(2 - \frac{8\lambda}{10\ Dq}\right)$$

where μ = observed magnetic moment in B.M.

μ_0 = spin only value 5.92 B.M.

α = A constant depending upon metal ion stereo-chemistry condom-shortley ligand field repulsion parameters F2 and F4 are calculated by low and Resengarton formulation (44).

$$C = \frac{35\ F4}{442} \quad \text{and} \quad B = \left(\frac{F2}{49} - \frac{5\ F4}{441}\right)$$

he free ion value of F2 and F4 iron (III) are 80.93 KK and 0.27 KK respectively, while the corresponding values for ron(III) complexes are in the range 90-105 KK; 59-65 KK espectively. Increase in F2 and F4 values are due to expanded adial functions of the d-electrons(45).

Carlo-Tosi (46) observed very weak spin forbidden ransition in high spin outer octahedral iron(III) complexes in he region 28170 - 29150 cm -1 and 37600 - 38750 cm -1, which get

splitted as well as ecpected to overlap. In the complexes under study bands observed in the range 27200-31500 and 36000-40880 cm -1 also get splitted as.

$$27200 - 31500 \text{ cm} -1; \text{ de} ---> \pi_4 \begin{cases} ---> dE(a) ---> \pi_4(a1) \ (\nu_\alpha) \\ ---> dE(e) ---> \pi_4)a1) \ (\nu_\beta) \end{cases}$$

$$36000 - 40880 \text{ cm} -1; (\pi_3 --> \pi_4) \begin{cases} > \pi_3(e) ---> \pi_4(e) \ (\nu_\alpha') \\ > \pi_3(az) ---> \pi_4(a1) \ (\nu_\beta') \end{cases}$$
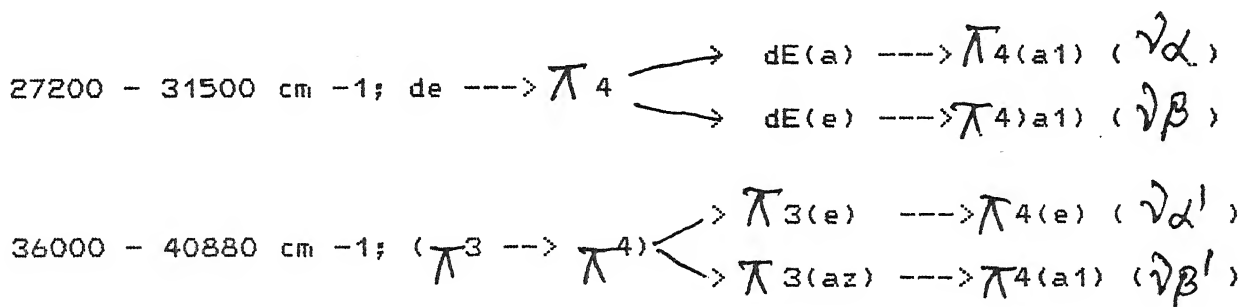
These splitted band $(\nu_\alpha + \nu_\beta)$ and $(\nu_\alpha' + \nu_\beta')$ have about the same energy and are expected to overlap.

<u>Infrared Studies</u>:- Ortho hydroxy benzaldehyde is a Vic - hydroxy aromatic aldehyde possess favourable features for the formation of stable five / six membered chelate ring with metal ions. The large repulsive effect of non polar portion of alkyl group outer weights the solubility effect of phenolic - OH group, therefore, they are insoluble in common solvents also they melt comparatively at high temperature because of intermolecular hydrogen bonding. The amine ring substituents do not seem to influence either the electron density or the bond order of the azomethine group, possibly due to the orbital overlap resulting from the non planar arrangement of the molecule (47). In substituted salicylaldehydes and amines the electronic interaction betweem the substituent is possible (48). During

Electronic spectral studies of the complexes it has been noticed that electron donating substituents in the O-amino benzophenone moiety and electron with drawing groups in the phenolic moiety increases the tendency of intermolecular association. Dudek and Dudek (40), on variety of Schiff basses observed that the phenolic proton resides predominantly on oxygen in N-aryl Schiff bases while N-alkyl Schiffs bases exist in the Cis-Keto form. The substituent which increase the basicity of the imine nitrogen or the acidity of phenolic proton favours the Cis-Keto form and Vice versa (50).

Present Schiff bases contain phenolic hydroxyl ortho to azomethine group, an intramolecular hydrogen bonding between phenolic hydroxyl and azomethine nitrogen as well as quinonoid formation is possible. A band around 400 nm. observable in the spectra of the complexes, suggest possible contribution from intra molecular hydrogen bonding as well as

Table (4.5) Important IR frequencies of substituted salicylidene amino benzophenone Iron (III) Complexes.

S.No	Complexes	ν_{OH} (C–O)	$\nu_{(C=N)}$ and NH Bending Plane	–CH Benzene in Plane	$\nu_{C=O}$	$\nu_{(M-N)}$	$\nu_{(M-O)}$
1	[Fe (C21 H16 NO3)2] cl.H2O	1340m	1580 vs	1400 w	1630 ms	510 m	450 m
2	[Fe (C22 H18 NO2)2] cl	1300m	1570 vs	1420 s	1640 vs	500 w	430 m
3	[Fe (C20 H13 NO2 cl)2] cl	1330m	1600 m	1400 ms	1650 m	500 w	450 m
4	[Fe (C22 H18 N1 O3)2] cl	1320m	1605 m	1420 s	1640 m	500 w	410 w
5	[Fe (C21 H16 NO3)2] (NH3)	1340m	1570 m	1420 s	1620 m	525 w	430 w
6	[Fe (C22 H18 NO3)2] 2NH3	1330m	1580 m	1420 s	1630 vs	510 w	410 w

Wave length (microns)

Wave number (cm⁻¹)

[Fe(C₂₁H₁₆NO₃)₂]Cl·H₂O

[Fe(C₂₂H₁₈NO₂)₂]Cl

[Fe(C₂₀H₁₉NO₂Cl)₂]Cl

[Fe(C₂₂H₁₈NO₃)₂]Cl

Transmittance (%)
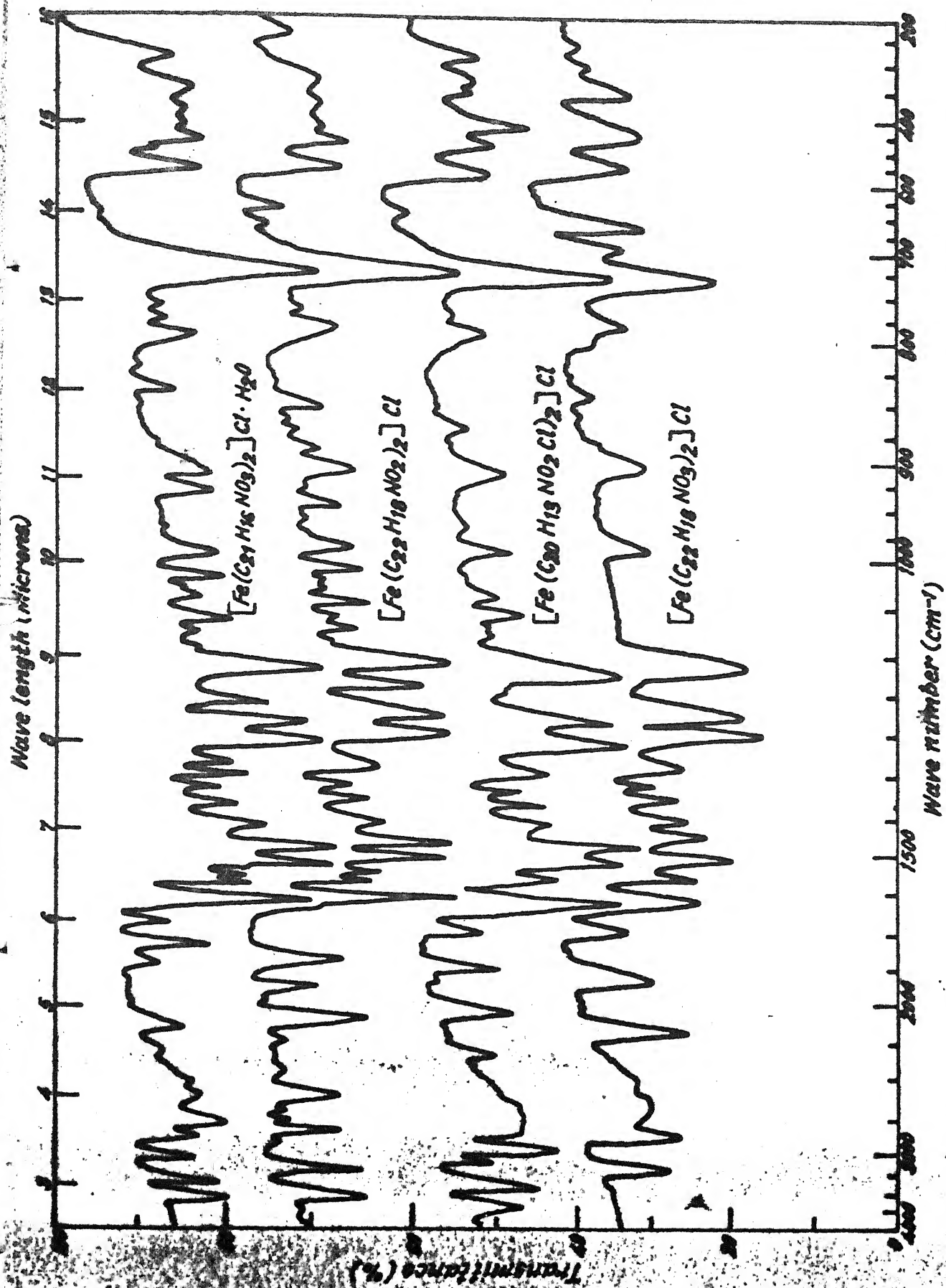
Fig. (4.1) : I.R. Spectra of Iron (III) complexes.

Quinonid   structures.   This   largely   depends   upon   t
substituents present. Because of Alkyl group there will be high
electron density around azomethine nitrogen compared to that
salicyl-aldehyde. The alkyl group has positive inductive effe
and   there is increase electron density at the nitrogen ato
hence phenolic proton will have higher ionisation energy(51), a
strong H-bonding . In 5-alkoxy salicylidene-O-amino benzophenc
since alkoxy froup is electron donating, it increases t
basicity of phenolic oxygen and hence will shield the phenol
proton.   Therefore   5-alkyl   salicylidene   amino   banzophenc
Iron(III) complex absorb at higher field. It is known that if t
same charge (positive or negative) on an ions increased it beco
less stable. The inductive effect of the phenyl ring will be mo
in salicyl-aldehyde consequently it will help in ionisation. Al
stronger the electron with drawing effect of the chloro stablis
the anion due to dispersal of negative charge favouring a hi
degree of ionisation.

Some   important   IR   bands of diagnostic   importance   a
discussed wich reveals hydroxyl group; azomethine and Keton
group as the possible reactive sites.

(i)   **Vibrations due to Ketonic group:-** The free $>C = O$ gro
in the ligasnds show vibration frequency 1680-1700 cm -1 which
complexation get decreased considerably showing the presence
coordinated Ketonic group (52). A large number of 'transiti

Wave length (Microns)

[Fe (C$_{21}$ H$_{16}$ NO$_3$)$_2$] (NH$_3$)

[Fe (C$_{22}$ H$_{18}$ NO$_3$)$_2$] (NH$_3$)$_2$

Transmittance (%)

Wave number (cm^{-1})
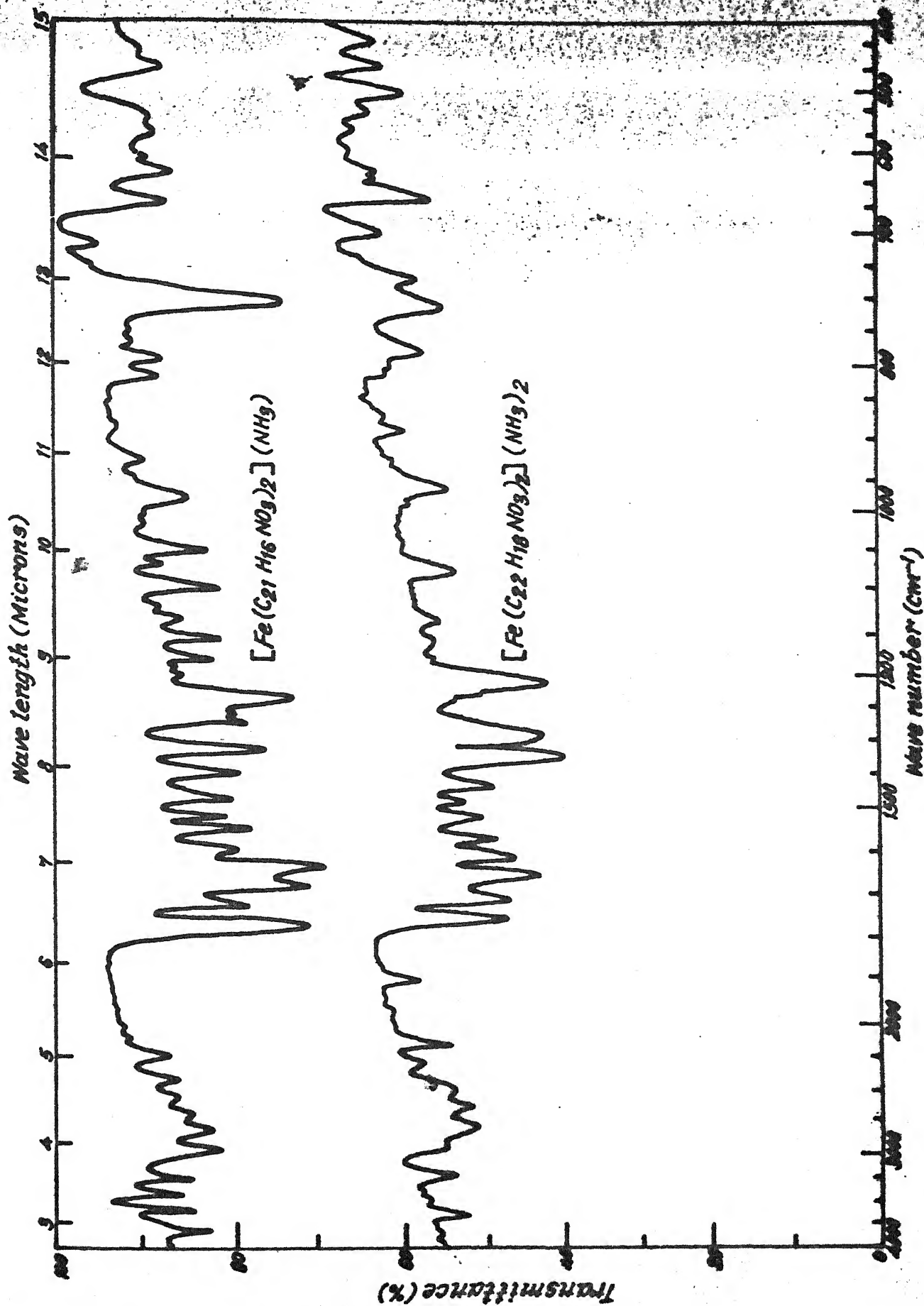
metal complexes with hetero cyclic Schiff base also reported similar type of observastion (53-56).

The presence of water of crystasllisation (57) is confirmed by the appearance of δ(O-H) in the region 3600-3500 cm -1 and ν(O-H) in the region 1600-1610 cm -1. A coordinated water gives-band at ~3200-3400 cm -1 due to (O-H) along with 1580 and 840 cm -1.

(ii) <u>Azomethine Linkage</u>:- IR spectrum of the free ligand exhibit hands in the region (1620-1640 cm -1) which is identified as (CH=N) linkage, and it undergoes a hypsochromic shift in the complexes suggesting possible coordination sites(58).

(iii) <u>Phenolic hydroxyl linkage</u>:- The IR spectrum of the free ligand, the bands appearing in the region 3000-31000 cm -1 and 2900 cm -1 have been assigned to νOH. This band disappear in the spectra of the complexes indicating the chelation via deprotonation of (OH) Phenolic group. Similar chelates asre found in metal Oximes(59-61). Appearance of band ~2900 cm -1 (expected due to phenolic -OH group) may be due to intramolecular hydrogen bonding between the hydroxyl hydrogen and nitrogen of the azomethine group forming a stable six membered ring. Phenolic ν(C-O) and δ(O-H) observed ~ 1270 cm -1 in the free ligand shifted to ~ 1340 cm -1 further suggest deprotonation of phenolic hydrogen (62-63). The hypsochromic shift of both these bands on complexation suggest coordination through oxygen.

The (Fe-N) and (Fe-O) modes appear in the region 500-550 cm -1 and 400-450 cm -1 respectively are in confirmity with literature report (64-68).

CHAPTER - IV

R E F E R E N C E S

1. V. Pekarek and V. Veseley - Talanta (1972), 19,1245.

2. P. Raman Murthy A. Radhakrishnan, R. Vijay Raghvan and P. Natrajan - Ind. J. Chem. 29 A (1990) P-1.

3. M. Qureshi, K.G. Varshney and A.H. Israili -J. Chromatog. (1971), 59, 141; (1972, 65, 247; J.Ind. Chem. Soc.(1981), 58, 241; Sepn. Sci. (1971), 6, 559.

4. G. Mclendon and A.E. Martell-Coord. Chem. Rev.19,(1976).

5. E. Natrajan and P. Natarajan-Inorg. Chem. Acta.155(1989).

6. B.E. Smith, D.J. Lower and R.C.Bray -Biochem. J.(1973, 135, 331.

7. W.G. Zumfit, L.E. Mortrson and G. Palmer -Eur. J. Biochem. (1974)m 46m 525.

8. P.K. Das and D.K. Sarkar -Ind. J. Chem. (1979) 17 A, 461, J.Ind. Chem. Soc. 58, 1135 (1981).

9. Sulekh Chandra and K.B. Pandey -Trans. Metal complexes 5 (1980) 80.

10. Bergen, A. Vanden, K.S. Murray, M.J. Oconnor, N. Rehak and B.O. West. Aust. J. Chem. 21, 754, 1505 (1986).

11. M. Gerloch, J. Lewis, F.E. Mabbs and A. Richards - J. Chem. Soc. (A) 112 (1968).

12. M. Gerloch, J. Lewis, F.E. Mabbs and A. Richards -Nature 212, 809 (1966).

13. J. Lewis, F.E. Mabb and A. Richards -J. Chem. Soc. (A) 1014(1967).

14. M. Gerloch, J. Lewis, F.E. Mabbs and A. Richards —Nature 212, 809(1966).

15. L.T. Taylor and R.D. Patton —Inorg. Chim. Acta 8, 191 (1974).

16. P.F. Lindley and A.W. White —Chem. Comm. 355 (1970).

17. F.G.A. Stone and R. West —Advances in organometallic chemistry, vol 13 (Academic Press, New York) 1964,82.

18. J.P. Collman and L.S. Hegedus —principles and applications of organotransition metal chemistry (Science Books) chapter 14(1980).

19. L. Sacconi —J. Chem. Soc. (A) 248(1970); Coord. Chem. Rev. 8, 351 (1972).

20. W.M. Coleman and L.T. Taylor —J.Inorg. Nucl. Chem. 33, 3049 (1971).

21. A.K. Rana and J.R. Shah—J. Ind. Chem. Soc. 63,281(1986).

22. B.N. Figgis and J. Lewis —Prog. Inorg. Chem. (1964), 6, 167.

23. E.L. Muetterties —Acct. Chem. Res. 3, 266 (1970); Rec. Chem. Prog. 31, 51 (1970).

24. W. Jolly —coord. Chem. Rev (1971) 13, 47.

25. M. Gerloch and R.C. Slade —"Ligand field parameters" Cambridge University press London (1973).

26. M. Ciampolini and M. Nardi —Inorg. Chem. 5,45,1150(1966).

27. W.J. Greary —Coord. Chem. Rev; (1971) 7, 81.

28.   W.V. Dahlhoff and S.M. Nelson —J. Chem. Soc. (A) 2184
        (1971).

29.   S.M. Nelson —Ann. Repts (Chem. Soc.) 71, 280 (1974).

30.   S.M. Nelson and T.R. Dick —Inorg. Chem. 8, 1208 (1969).

31.   P.C. Srivastava —Ind. Jour. of Chem. 29A (1990) P 75.

32.   J.P. Collman and C.A. Reed —J. Am. Chem. Soc. 95, 2048
        (1973).

33.   E.M. Nour, L.H. Chen and J. Laane —J. Raman spectrosc.
        17 (1986) 467.

34.   L.F. Lindoy — Chem. Soc. Rev. 14, 421 (1975).

35.   R. Faggiani, R.J. Gillespie, C. Campana and J.W. Kolis
        — J. Chem. Soc. Chem. commun (1987) 485.

36.   Y.D. Kulkarni, S. Srivastava and M. Athar —Ind. J. Chem.
        25 A (1986) 57.

37.   N.W. Alcock, D.C. Lills, M. Mcpartlin and P.A. Tasker
        — J. Chem. Soc. Dalton 727 (1974).

38.   James, Wrobleski and G.J. Long — Inorg. Chim, Acta 36
        (1979) 155.

39.   S.L. Chadha and Kamini Uppal — Ind. J. Chem. 29 A (1990)
        80.

40.   Chem Dian and A.E. Martell — Inorg. Chem. 26 (1987)1026.

41.   S.L. Chadha and V. Sharma — Z. Anorg. Allg. Chem. 545C
        (1987) 227.

42.   P.K. Radha Krishnan — Polyhedron 5 (1986) 995.

43.   B.N. Figgis —" Introduction to Ligand field Theory " —
        McGraw Hill N.Y. (1966).

44.(a)   M.Iida and H.Yamatera- Bull. chem.Soc. Japan (1981) 54,441.

44.(b)   W.Low and G.Rosengarten-Jour. Mol. Spectra 12 (1964). 319.

45.   R.C.Saxena and C.L.Jain -Curr. Sci. 47 (1978, 328 and 766.

46.   Carlo, Preeti and G.Tosi -Aust. Jour. chem.33 (1980) 1203.

47.   S.Patai - "The chemistry of carbon, Nitrogen double bond" (Interscience New York (1970).

48.   Hemlatha Ranganathan, T.Ramaswami. D.Ramaswamy and M.Santappa - chem. Lett. (1977) 1201; Curr. Sci. (1978) 330; Ind.J.chem. 25A. 127 (1986).

49.   G.O.Dudek and E.P.Dudek -. Am. chem. Soc. (1966) 88.2407

50.   W.Ledbetter John (jr) - J.Phys. chem. (1966), 70 2245; (1967); 71, 2351.

51.   S.K.Srivastava - Ind. J.chem. Sect (A) (1978) 16, 88.

52.   K . Nakamato- " Infrared spectra of Inorganic and coordination compounds" John Willey new York (1970)p.175

53.   P.R. Shukla, Suresh chand and G. narain - Jour. Ind. chem. Soc. 63, 333 (9186): 60, 291,321,287, 397, 788, (1983).

54.   P.K.Kanungo, N.K.Sankhla and R.K.Mehta - Jour. Ind. chem. Soc. 63, 335 (1966).

55.   J.P.Tondon and Anil Varshney - Ind. Jour. of chemistry 25 A, 191 (1986) 24 A, 70 (1985).

56.   M.A.Ali. S.E.Livingstone and D..Philips - Inorg. chim.

Acta 5 (1971) 119.

57.   B.N.Cyvin,   S.J.Cyvin,   A.Zabokrzycka   and   B.B.Kedzia
       spectrosc. Lett. 16 (1983) 249.

58.   J.P.Tondon, R.V.Singh and R.D.Shora - Ind.   J.chem. 25A
       188 (1986).

59.   P.P.Bhargava and Mala Tyagi - Ind.   J.   chem.   25A   193
       (1986).

60.   N.S.Birada and V.B.Mahale - J.   Less.   Common metal   31
       (1973) 159: J.Inorg. nucl. chem. 35 (1973), 2565.

61.   J.Kaufmann and F.Kober - J. Organo metal chem. 99. (1975) 33.

62.   F.Teyssie and J.J.Charette - Spectro chim.   Acta.   (1963) 19
       1407.

63.   D.M.Adams - "Metal Ligand and related vibrations" - Edwar
       Arnold London. (1967).

64.   D.P.Brown - Inorg. chem. 14 (1975) 2582,, Inorg. chim. Acta.
       (1971) 314.

65.   P.G.Rasmussen and S.Meyers - Polyhedron 3, (1984) 183.

66.   S.Das , R.N.Banerjee and D.Banerjee - J. Coord. chem. (1984
       13, 123.

67.   D.Banerjee _ Jour. Ind. Chem. Soc. 67 (1990) 286.

68.   Shekhar Srivastava, Shraddha Srivastava and Anjulata Sharma
       Jour. Ind. chem. Soc.. 67 (1950) 310.

CHAPTER --- V

Stereo chemical studies on octahedral and square planar complexes of copper (II), Manganese (II) and Uranyl (II) with 2:5- Dimethoxy phenyl glyoxal thiosemicarbazone and 4-p- methoxy phenyl thiosemicarbazone of 2:5 Dimethoxy phenyl glyoxal.

Introduction:- Preparation and characterisation of molecules contaning polymetallic copper has evoked much interest in recent years (1-6). Binuclear complexes being the simplest of such polynuclear centres there has been a steady increase in the number and variety of such compounds studied . The magnnetic moments of five coordinate copper (II) complexes are generally in the range reported for d9 system in four or six coordinate complexes (7-8) i.e. 1.85-2.10 B.M. The magnetic properties of copper (II) complexes have been reviewed. (9-11). In general , these complexes have been found to obey the curie weiss law, but in some cases variation of magnetic moment with temperature has been observed (12). The lowering of μeff, value has been attributed to exchange coupling.

Diverse biological activities have been found in compounds having the phenyl glyoxal moiety. Electronic configuration (3d5) has the possibility of existing in three possible spin states (S= 5/2,3/2, and 1/2). Complexes with spin sextet and doublet ground states give rise to magnetic moments corresponding to five unpaired electrons in the range 5.80-6.0 B.M. Seeveral high spin manganese (II) complexes are known to have normal values of μeff. The stability constants of the chelates of 4-(o-methoxy phenyl) thio-semicarbazide (16) have been studied by Saxena et.al. Here we wish to present the result

of our studies on copper (II), Manganese (II) and uranyl complexes with 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone and 4-p- methoxy phenyl thio semicarbazone of 2:5 Dimethoxy phenyl glyoxal. The transition metal ions used in the present investigations are also of biological importance (18).

Experimental:- 1. [Cu (C11 H13 N3 O3 S)3] Cl2 Dark greenish colourprecipitate was obtained by mixing ethanolic solution of CuCl2. H2O (0.8555 gm. 0.05M) 2:5 Dimethoxy phenyl- glyoxal thio-semicarbazone (0.025 M) dissolved in ethanol in 1:2 ratio. The mixture was refluxed for about two hours over water bath and on subsequent cooling greenish mass was prepared. It was filtered, washed with water ethanol and dried in an air oven.

2. [Cu(C11 H13 N3 O3 S)2]Cl2- Alcoholic solution of liquid ammonia d do.88) was dropped to attain pH 6.5 into the reaction mixture obtained by mixing 2:5 Dimethoxy phenyl glyoxal thio semicarbazone and cupric chloridedissolved in ethanol in a ratio of 1:2 when Buff green colour mass was obtained, after refluxing the contents over water bath for about an hour. It was filtered, washed and dried as before.

3. [CU2 (C19 H19 N3 O4 S)2]Cl4 - Greenish coloured reaction mixture was obtained by mixing hot ethanolic solution of cupric chloride dihydrate (0.85 g, 0.005 M) and ligand (4p-methoxy phenyl thiosemicarbazone of 2:5 dimethoxy phenyl glyoxal) (0.005M) dissolved in the same solvent, and heated over a water bath for two hours . The greenish solid obtained was collected on a filter paper under suction washed with water ethanol mixture as usual.

4. [Mn (C11 H13 N3 O3 S)2Cl2] -- Solution of 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone (0.005M) in ethanol and MnCl2 . 4 H2O (0.98 g , 0.005 M) in ethanol water (25 ml) were mixed together and content was refluxed for about an hour, on a water bath. The pinkish solid obtained was collected on a filter paper under suction, washed with water ethanol mixture and dried.

5. [Mn (C11 H13 N3 O3 S)2 (NH3)2]-- To a 1:2 ethanolic solution of MnCl2. 4 H2O and the 2:5 Dimethoxy phenyl glyoxal thio semicarbazone few ml. of alcoholic solution of ammonia was added to attain 6.5 pH. The reaction mixture was stirred and refluxed for 1 Hr. A pinkish mass was obtained, filtered and washed with water, and dried under vacuo over P4O 10 to form the desired compound.

6. [Mn2(C19 H19 N3 O4 S)2 Cl4]---- Light pink colour metal complex was isolated by refluxing ethanolic solution of the MnCl2.4 H2O and 4-p- methoxy phenyl thio semicarbazone of 2:5 Dimethoxy phenyl glyoxal in 1:1 molar ratio for two hours. The insoluble complex was filtered washed with water dried in vacuum and analysed for the percentage of the metal, C, H, and N, micro analytically.

7. [UO2 (C11 H13 N3 O3 SO2] (CH3 COO)2 -- Alcoholic solution of uranyl acetate (2.120 gm. 0.005 M) and 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone was mixed together in 1:1 molar ratio. the content was refluxed for about an hour and then concentrated and cool to obtain the yellow colour mass.

8. [U2(C11 H13 N3 O3 S)2](NO3)2 -- Yellow coloured solid was obtaind by reacting uranyl nitrate hexahydrate (2.51gm 0.005M)

and 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone (M=L ; 1:2) in ethanol solution, after refluxing the mixture for about an hour.

9.   [(Uo2)2 (C19 H19 N3 O4 S2](NO3)4-- Brownish yellow coloured precipitate forms after refluxing the mixture containing uranyl nitrate hexahydrate and 4-p-methoxy phenyl- thiosemicarbazone of 2:5 Dimethoxy phenyl glyoxal in 1:1 molar ratio for 2 hours. The product was filtered off, washed with water and finally dried in a desiccator over fused calcium chloride.

Table (5.1) Analytical and magnetic date of Copper (II) Complexes.

S.No.	Compound (Colour)	Chemical analysis calcd/ (Found)						Magnetic Data		Stereo chemistry
		C	H	N	S	Cl	Metal	X 1 mx 10^-6 C G S Unit	Neff (B.M) Unit	
1	[cu (C 11 H13 N3 O3 S)3] cl2 (Green)	42.32 (42.07)	4.16 (3.92)	13.46 (13.08)	10.26 (9.83)	7.58 (9.10)	6.79 (6.20)	1517.61	1.91	Distorted octahedral
2	[(cu (C 11 H13 N2 O3 S)2] cl2 (Buff green)	39.48 (39.00)	3.88 (3.28)	12.56 (12.12)	9.57 (9.21)	10.62 (9.83)	9.50 (9.00)	780.67	1.37	Sq.planar
3	[cu2 (C19 H19 N3 O4 S)2] cl4 (Greenish)	43.85 (43.18)	3.65 (3.15)	8.07 (8.01)	6.15 (6.05)	13.65 (13.03)	12.22 (11.75)	1822.52	2.1	octahedral

Table (5.2) Analytical and magnetic date of Manganese (II) Complexes.

S.No.	Compound (Colour)	Chemical analysis calcd/ (Found)						$X \ 1 \ mx \ -6 \ 10$ Cgs Unit	μ_{eff} (B.M)	Stereo chemistry
		C	H	N	S (Anion)	Cl (Anion)	Metal			
1	[Mn (C 11 H13 N3 O3 S)2] cl2 (Pink)	40.00 (39.62)	3.93 (3.22)	12.72 (11.88)	9.69 (9.38)	10.75 (10.02)	8.32 (8.00)	14289.93	5.84	High spin octahedral
2	[Mn (C 11 H13 N3 O3 S)2 (NH3)2] (Pink)	44.37 (41.80)	5.13 (4.83)	17.99 (17.17)	10.27 (9.65)	– –	8.82 (8.27)	14100.34	5.8	High spin octahedral
3	[Mn2 (C19 H19 N3 O4 S)2 cl4] (Light Pink)	44.62 (44.00)	3.71 (3.12)	8.22 (8.05)	6.26 (5.95)	13.89 (12.65)	10.75 (9.85)	14943.03	5.75	High spin octahedral

Table (5.3) Analytical and magnetic date of uranyl – Complexes.

S.No.	Compound (Colour)	Chemical analysis calcd/ (Found)					X 1 mx $-\mu_{eff}$ 10 Cgs Unit	μ_{eff} (B.M)	Stereo chemistry
		C	H	N	Metal	Anion			
1	[Uo2(C11 H13 N3 O3 S)2](CH3COO)2 (Yellow)	33.83 (32.75)	3.47 (3.07)	9.11 (9.35)	24.94 (23.55)	12.79 (11.88)	161.05	0.62	High spin octahedral
2	[Uo2(C11 H13 N3 O3 S)2] (NO3)2 (Yellow)	28.44 (27.67)	2.80 (2.15)	15.08 (14.73)	25.64 (24.17)	13.36 (12.65)	229.53	0.75	High spin octahedral
3	[(Uo2)2 (C19 H19 N3 O4 S)2](NO3)4 (Brownish yellow)	29.26 (28.85)	2.48 (2.30)	8.98 (8.01)	30.55 (29.87)	15.91 (14.80)	340	0.86	High spin octahedral

Table (5.4) Electronic spectral absorption bands, Tentative assignments and relevent ligand field parameters for Mn (II) complexes

No.	Compound	Absorption bands CM-1	Tentative assignments	Relevent Ligand field parameters						
				B	10Dq	F_2 k.k.	F_4 k.k.	β_{35}	hx	x/Z
1	[Mn(C11 H13 N3 O3 S)2 Cl2]	18300	$6A1g \longrightarrow 4 T1g(G)$	762.5	8380	58.71	38.43	0.794	2.807	1.47
		22640	$\longrightarrow 4 T2g(G)$							
		25170	$\longrightarrow 4 A1g(G).4Eg(G)$							
		28830	$\longrightarrow 4 T2g(D)$							
		34760	$\longrightarrow 4 T1g(P)$							
2	[Mn(C11 H13 N3 O3 S)2 (NH3)2]	19000	$6A1g \longrightarrow 4 T1g(G)$	791.66	8704	60.92	39.89	0.824	2.837	1.50
		23200	$\longrightarrow 4 T2g(G)$							
		25180	$\longrightarrow 4 A1g(G).4Eg(G)$							
		29070	$\longrightarrow 4 T2g(D)$							
		35300	$\longrightarrow 4 T1g(P)$							
3	[Mn2(C19 H19 N3 O4 S)2 Cl4]	18000	$6A1g \longrightarrow 4 T1g(G)$	750	8250	57.74	37.8	0.756	2.769	1.53
		22100	$\longrightarrow 4 T2g(G)$							
		25030	$\longrightarrow 4 A1g(G).4Eg(G)$							
		28800	$\longrightarrow 4 T2g(D)$							
		34900	$\longrightarrow 4 T1g(P)$							

Table (5.5) Electronic spectral absorption bands, and their assignments for Cu (II) /Uo2 (II) complexes.

Page no. 88

S.No.	Compound	observed bands in cm-1			charge-Transfer bands	Stereochemistry
		2A1g (ν_1)	2Eg (ν_2)	2B2g 2 B1g --->		
1	[Cu (C11 H13 N3 O3 S)3]Cl2	15300			23200	Distorted Square planar
2	[Cu (C11 H13 N3 O3 S)2]Cl2	2A1--->2E 2E$_x$--->E	7300 17450		20600	Distorted Octahedral
3	[Cu2 (C19 H19 N3 O4 S)2]Cl4	7200 16890				Distorted Octahedral

		(1)	(4)	(2)	(7)	(3)	(5)	(8)	(6)
			R(UO)A		ν_s(OUo)Cm-1		ν_{as}(OUo) Cm-1	fUO Octahedral m.dynes/A	
4	[Uo2(C11 H13 N3 O3 S)2](CH3COO)2	19900	1.1933	36400	830	44200	900	Octahedral	6.57552
5	[Uo2(C11 H13 N3 O3 S)2](NO3)2	20200	1.17746	36700	810	44310	880	Octahedral	6.42243
6	[(Uo2)2(C19 H19 N3 O4 S)2](NO3)4	20010	1.178	36600	800	43905	890	Octahedral	6.42266

Table (5.6) Thermo-analytical data of copper (II) complexes.

S.No	Complex	Sample wt. (mg)	Residual wt. (mg)	Q_c 140 – 180 Thero. Expt.	Mass loss % 200– 320 Thero. Expt.	Residual 410–600 Thero. Expt.
1	[Cu(C11 H13 N3 O3 S)3]Cl2	85 mg	53.64	NIL	10.35 12.14	60.37 61.27
2	[Cu(C11 H13 N3 O3 S)2]Cl2	110 mg	64.72	NIL	9.39 10.22	82.19 83.10
3	[Cu2(C19 H19 N3 O4 S)2]Cl4	60 mg	38.78	NIL	7.72 8.15	35.36 36.11

Table (5.7) Thermo-analytical data of Mn (II) complexes.

S.No	Complex	Sample wt. (mg)	Residual wt. (mg)	40 - 180 Thero. Expt.	Mass loss % 210- 380 Thero. Expt.	Residual 400-630 Thero. Expt.
1	[Mn(C11 H13 N3 O3 S)3]Cl2	75	30.31	NIL	9.20 10.01	12.20 13.33
2	[Mn(C11 H13 N3 O3 S)2(NH3)2]	125	65.48	NIL	8.11 9.77	98.77 99.02
3	[Mn2(C19 H19 N3 O4 S)2Cl4]	135	82.75	NIL	20.46 22.14	93.69 94.22

Table (5.8) Thermo-analytical data of Uo2 (II) complexes.

S.No	Complex	Sample wt. (mg)	Residual wt. (mg)	Residual wt. 40 – 170		Mass loss % 170– 300		Residual 330–620	
				Thero.	Expt.	Thero.	Expt.	Thero.	Expt.
1	[Uo2(C11 H13 N3 O3 S)2](CH3COO)2	85	35.58	NIL		11.77	12.44	41.29	42.10
2	[Uo2(C11 H13 N3 O3 S)](NO3)2	120	64.77	NIL		15.34	16.60	51.23	52.41
3	[(Uo2)2(C19 H19 N3 O4 S)2](NO3)4	60	31.12	NIL		10.61	11.88	27.82	28.55

Result and discussion:-

(a) Magnetic measurement studies-

Distorted Square planar with tetragonal distortions

The magnetic moment value for copper (II) comlexes should be close to 1.78 B.M. irrespective of the nature of bonding involved however these values seldom provide much information about the stereochemistry. Therefore the low effective magnetic moment found for [Cu(C11 H13 N3 O3 S2]Cl2 (1.37. B.M) can be considered due to the formation of dimeric/polymeric molecules which lead to the presence of exchange coupled anti-ferromagnetisem in the complex either (19-22) through (Cu+2 - Cu+2) interaction or through ligand participation.

(b) **Distorted octahedral compound:-** The room temperature magnetic moment observed for [Cu (C11 H13 N3 O3 S)3] Cl2 (1.91) ; and [Cu2(C19 H19 N3 O4 S)2]Cl4 (2.10 B.M). The value is slightly higher than that expected for metal ion containing one unpaired electron. This difference in magnetic moment is attributed to orbital contribution forming distorted octahedral symmetry. (23).

Electronic spectral studies:-

(a) **Distorted square planar with Tetragonal distortions:-** In tetragonal geometry three transitions of the position $dx^2-y^2 \longrightarrow dxy$; $dx^2-y^2 \longrightarrow dz^2$ and $dx^2-y^2 \longrightarrow dzx.dyz$, are obserablebut generally these transitions over lap each other giving rise to one broad absorptions band. (24) [Cu (C11 H13 N3 O3 S)2] Cl2 exhibit three (d-d) transitions alongwith one charge transfer transition, in the visible region and tentatively assigned as given below-

15300 cm-1 $2\ B_{1g}$ ---> $2\ A_{1g}$ (ν_1); (dx^2-y^2 ---> dx^2)

17750 cm-1 $2\ B_{1g}$ ---> $2\ E_g$ (ν_2); (dx^2-y^2 ---> dxy. dy^2)

20600 cm-1 $2\ B_{1g}$ ---> $2\ B_{2g}$ (ν_3); ($dx^2-y^2\_$ ---> dxy)

23200 cm-1   -------> charge transfer band.

The intensity of the ν_1 band was found to be low as compared to other two transition (ν_2 and ν_3). It is reported (25) that distorted Cu (II) complexes exhibit one broad absorption band around 14.5 - 15.3 KK regions (26-27). in the above complexes transitions similar to distorted octahedral copper (II) complexes are observed, suggesting distortion in octahedral geometry

(b) **Distorted octahedral complexes:**

The complexes [Cu (C11H13N303S)3]Cl2 and [Cu2 (C19H19N304S)2] Cl4 exhibits two bands in the region 7000 - 7500 and 16000 - 18000 cm -1, tentatively assigned to 2 A1 --> 2 E and 2 Eg --> 2 E transition respectively as certaning distorted octahedral micro symmetry of the organic compounds around Cu(II) ion.2 Eg state is highly susceptible to Jahn Teller distortion. Third band which appear as103 a shoulder around 26000 cm -1 is belived to be a charge transfer band. These bands have been assigned to dxz. dyz--> dx2-y2 and dxy--> dx2-y2 transitions respectively as reported earlier(28-30) Tsuchida(31) and coworkers indicated that all the copper complexes in which the paramagnetism is partially or completely quenched absorb around 26000 cm -1. From the above studies it may be concluded that in copper (II) complexes, bands correspond to octahedral geometry, Further the results are consistent with an octahedral d9 system with considerable Jahn-Teller distortion. It is also reported that green or blue Cu(II) complexes are tetra-gonally distorted.

(a) _____ of Mn(II) complex.:- The effective magnetic moment of the ___ in (C11H13N3O3S)2 Cl2]; [Mn (C11H13N3O3S)2 (NH3)2] and [Mn2 (C19H19N3O4S)2 Cl4] complexes are 5.84, 5.80 and 5.75 B.M. respectively predicted for spin free d5 system with a 6A1g ground term, having high spin octahedral micro symmetry of the ligands around manganese(II) ion.

(b) Electronic spectral studies:- The spectra of Mn(II) complexes show five bands in normally expected region for Mn(II) octahedral complex, which are assigned (35) as below-

6 A1g --> 4 T1g (G) ~ 18000-19000

6 A1g --> 4 T2g (G) ~ 22000-24000 cm -1,

6 A1g --> 4 Eg, 4 A1g (g) ~ 24000-26000 cm -1;

6 A1g --> 4 T2g (D) ~ 28000-29000 and 6 A1g --> 4 T1g(p) ~ 34000-35000 cm -1

The 6 A1g --> 4 A1g, 4 E(G) transition energy can be estimated as 6 S --> 4 G, separation energy.

For 3 d transition metal the variation of Racah inter electronic repulsion parameters with the cationic charge (zx) and the number 'q' of electrons in the partly filled d- sub shell is expressed by the relation (33,34).

$$B = 384 + 58q + 124 (zx + 1) - \frac{540}{(zx + 1)}$$

where B is in cm -1, Lower value of B show the reduction in effective positive charge with cation and with an increased tendency to be reduced to lower oxidation state, The effective cationic charge (zx) for the [Mn(C11H13N3O3S)2 Cl2]; [Mn(C11H13N3O3S)2 (NH3)2] and [Mn2(C19H19N3O4S)2Cl4] complexes

are found to be 1.4732; 1.5011; and 1.5312 respectively, which is considerably lower than the formal +2 oxidation state of the metal. The values of Dq and B have been calculated by the linear relation

$$\frac{6\ A_{1g} \longrightarrow 4\ T_{1g}\ (G)}{B} = 24.00; \quad \frac{Dq}{B} = 1.1$$

Slater − condon shortley repulsion parameters F2 and F4 are also evaluated by the relation.

$$B = \frac{F2}{.49} - \frac{5\ F4}{441} \quad \text{and} \quad C = \frac{35\ F4}{.441} \quad \text{and} \quad C = 4\ B$$

and found to be 58.71; 38.43 complex I; 60.92; 39.89 complex II; 57.74; 37.80 complex III respectively which are in agreement with the previous work(35-36). Decreased value of B is considered due to an increased distance between electrons and thus an effective increase in the size of the orbitals.

Uranyl complexes, Magnetic and Electronic spectral studeis:- The uranyl complexes $[UO_2 \ (C_{11}H_{13}N_3O_3S)_2] \ (CH_3COO)_2;$ $[UO_2(C_{11}H_{13}N_3O_3S)_2] \ (NO_3)_2$ and $(UO_2)_2 \ (C_{19}H_{19}N_3O_4S)_2] \ (NO_3)_4$ possess magnetic moment value of 0.62, 0.74 and 0.86 B.M. respectively indicate that the complexes are diamagnetic as expected for 5 F0 system, although a totally symmetric ground state has been ascribed to the orbital contribution due to the involvement of uranium −5f− electrons in coordination(37).

Diffused reflectance spectra of the uranyl complexes exhibits three bands which are tentatively assigned(38) to 19000-21000 cm −1 (γ_1); Transiton with in the Uranyl ions 36000-38000 cm −1 (γ_2); Ligand −−> uranyl(II) charge transfer transitions. 43000-45000 cm −1 (γ_3); Intra ligand transitions of the organic molecule or n −−> π^x in the organic molecule.

The electronic spectral band around 2000 cm -1 is due to 1 Eg $+$ $\longrightarrow$ 3π Utransition typical of OUO symmetric stretch frequency for the first excited state(39).

The complexes exhibits a strong band at 880-900 cm -1 characteristic of as (O=U=O). The·force constant (f) values for γ_{as} (O=U=O) agree well with the values reported by earlier workers(41). The (U-O) bond length has been calculated with the help of the equation(42). R(U-O) = 1.17 + 1.08 f $-1/3$. The R(U-O) in the complexes is in the range (1.17 to 1.19 AO) and the values are comparable to those (1.60-1.92 AO) observed for some other Dioxouranium complexes(43). The γ_{s} (O=U=O) stretch occurs in the region 800-830 cm -1. The complex UO2 L2 exhibited a strong absorption at 260 cm -1 attributable to (UO2) bending mode. The formation of (M-N) and (M-O) bonds was further supported by the appearance of $\gamma_{(M-N)}$ and $\gamma_{(M-O)}$ in the regions 460-540 and 350-440 cm -1 respectively in metal complexes.

Thermo Gravimetric Analysis:-

Thermo gravimetric analysis has widely been used in the determination of structures of various metallic salts and complexes(44-45). By this method stability of the complex and hydration of the complex is determined.

Schematic representation of pyrolysis of copper(II) complexes:-

(a)   (1) [Cu(C11H13N3O3S)3] Cl2   (2) [Cu(C11H13N3O3S)2] Cl2
       and   [Cu2(C19H19N3O4S)2] Cl4.

(1) [Cu(C11H13N3O3S)2] Cl2 $\xrightarrow[- 2Cl]{210-340\,^{o}C}$ [Cu(C11H13N3O3S)2]

$\xrightarrow[- 2 L]{430 - 610\,^{o}C}$ Cu $\xrightarrow{[O]}$ Cuo

$(2) . [Cu(C_{11}H_{13}N_3O_3S)_3] Cl_2 \xrightarrow[- 2 Cl]{170-330 °C} [Cu(C_{11}H_{13}N_3O_3S)_3]$

$\xrightarrow[- 2 L]{410-620 °C} Cu \xrightarrow{[O]} Cuo$

$(3) . [Cu_2(C_{19}H_{19}N_3O_4S)_2]Cl_4 \xrightarrow[- 4 Cl]{170-360 °C} [Cu_2(C_{19}H_{19}N_3O_4S)_2]$

$\xrightarrow[- 2L]{400-610 °C} Cu \xrightarrow{} Cuo$
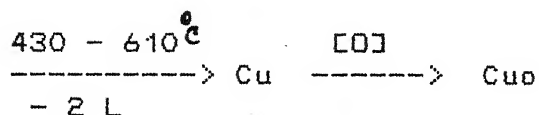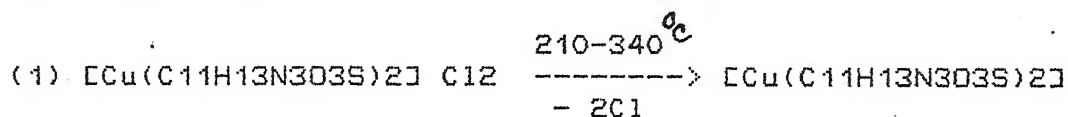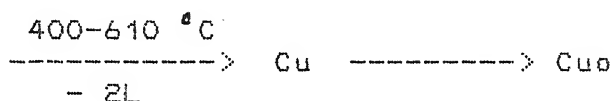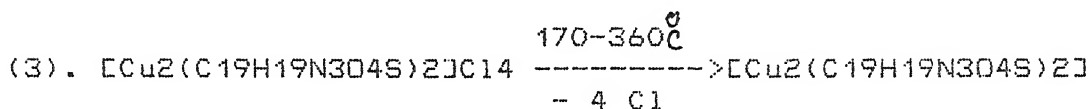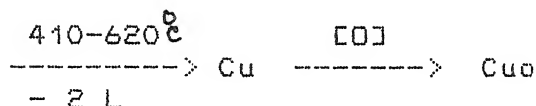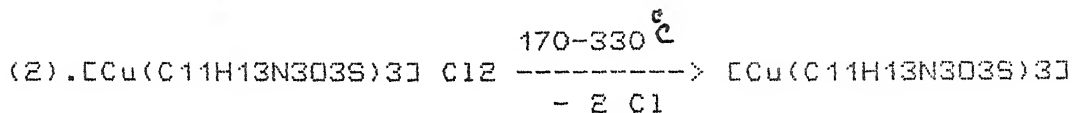
From thermogravimetric curves the horizontal lines indicates thermal stability of the complexes upto ~ 210 C with no loss in weight, above this temperature a small weight loss was observed in the temperature range 220-340 C. This may be due to the loss of chlorine molecules. By further raising the temperature no loss in weight is noticed, this shows thermal stability of the complex and strong coordination sites of the organic molecules. However by raising the temperature beyond 430 C a heavy loss in weight is observed which indicate the oxidation of the organic part of the compound into carbon dioxide and water, with the formation of metal oxide cupric oxide at the end of the reaction, and no loss in mass was noticed beyond 610 C.

DTA curves show medium endothermic peaks at 270 and 410 C (complex I); 270 and 390 C complex (II) and 230 and 430 C complex(III) and very strong exothermic peaks at (490 and 520; 470, 520 C and 490 and 530 C) for compounds 1,2, and 3

respectively. These exothermic peaks may account the formation of So2, CO2, and Nitrogen oxide while endothermic peaks at around ~ 24 can be considered due to the loss of chlorine as well as HCL molecule, while second peak observed in the range ~ 340 C may be subsequently represent the abrupt decomposition of organic compound.

1. [Cu(C11H13N3O3S)3] Cl2   Amount taken -85 mg. Endopeaks- 270 and 410 C; Exopeaks-490 and 530 C.

2. [Cu(C11H13N3O3S)2] Cl2   Amount taken -110 mg. Endopeaks- 270 and 390 C. Exopeaks- 470 and 520 C.

3. [Cu2(C19H19N3O4S)2] Cl4   Amount taken -60 mg. Endopeaks -230 and 430 C; Exopeaks -490 and 530 C.

Manganese (II) complexes:-

(b) (1). [Mn(C11H13N3O3S)2. Cl2] (2). [Mn(C11H13N3O3S)2 (NH3)2]
     (3). [Mn2(C19H19N3O4S)2 Cl4]

The horizontal line on (TG) came upto 180 C shows the thermal stability of the complexes. Poor thermal stability of the complexes is due to weak coordination sphere. This also suggest the absence of bridging of halogen moieties between the manganese ions in a single complex molecule. Small weight loss are observed in the temperature range 140-300 C, indicate the liberation of ammonia and chlorine molecules. Further heavy loss in weight was reported above 415 C, showing combustion of the organic part of

the molecule in presence of oxygen to form the oxide Mn_2O_3. This may be contaminated with higher oxide Mn_3O_4 also.

DTA curves show endothermal effect at 160 , 205 and 435 C, showing liberation of ammonia, chlorine molecules and decomposition of organic compound. At higher temperature some exothermal peaks are observed in the range 410-580 C, exhibiting the combustion of the complex organic part, with the formation of CO_2, H_2O etc.

Schematically thermal decomposition is given below:-

1. $[Mn(C_{11}H_{13}N_3O_3S)_2 \ Cl_2$ $\xrightarrow{40-180°C}$ $[Mn(C_{11}H_{13}N_3O_3S)_2 \ Cl_2]$

$[Mn(C_{11}H_{13}N_3O_3S)_2 \ Cl_2$ $\xrightarrow[-2\,Cl]{140-370\ C}$ $[Mn(C_{11}H_{13}N_3O_3S)_2$ $\xrightarrow[-2\,L(O)]{410-600}$

$Mno \longrightarrow Mn_2O_3$.

2. $[Mn(C_{11}H_{13}N_3O_3S)_2 \ (NH_3)_2]$ $\xrightarrow{40-180\ C}$ $[Mn(C_{11}H_{13}N_3O_3S)_2 \ (NH_3)_2]$

$\xrightarrow[-2NH_3]{210-370}$ $Mn(C_{11}H_{13}N_3O_3S)_2$ $\xrightarrow[[O]]{410-620\ C}$ Mno $\longrightarrow Mn_2O_3$

3. $[Mn_2(C_{19}H_{19}N_3O_4S)_2 \ Cl_4]$ $\xrightarrow{40-160}$

$[Mn_2(C_{19}H_{19}N_3O_4S)_2Cl_4]$ $\xrightarrow[-4Cl]{210-370}$ $[Mn_2 \ (C_{19}H_{19}N_3O_4S)_2]$

$| -2L(O)$

$| \ 430-600\ C$

Mn_2O_3 $\longleftarrow$ Mno
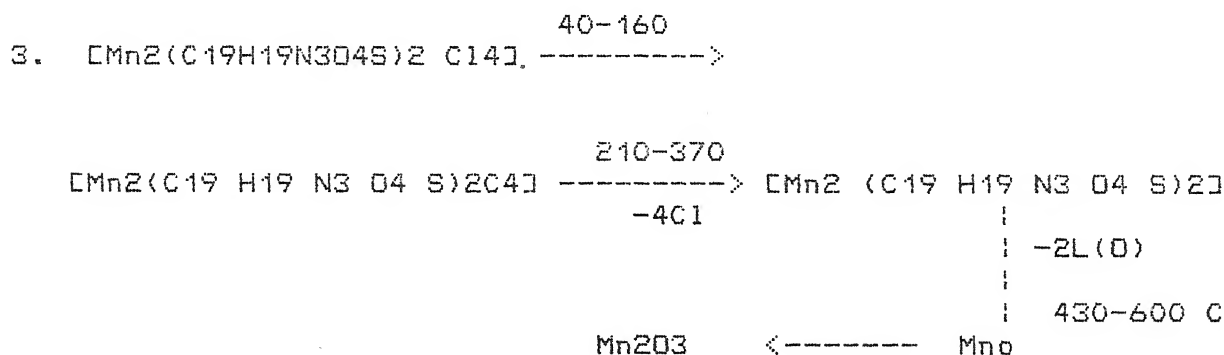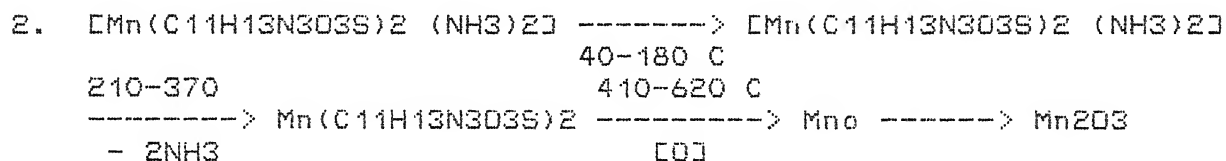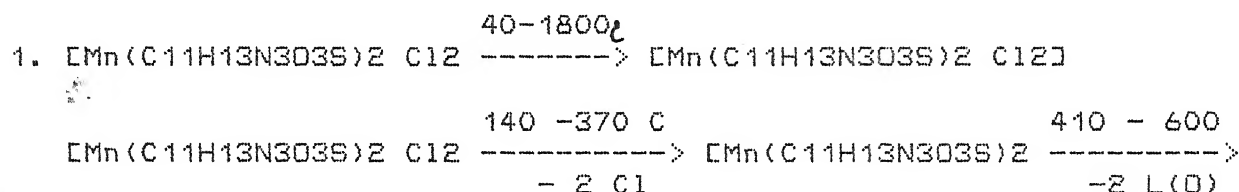
(c) <u>Uranyl (II) complexes</u>:-

(1). $[UO_2(C_{11}H_{13}N_3O_3S)_2](CH_3COO)_2$　　(2). $[UO_2(C_{11}H_{13}N_3O_3S)_2](NO_3)_2$

(3). $[(UO_2)_2(C_{19}H_{19}N_3O_4S)_2](NO_3)_4$

From TG curve the thermal stability of the uranyl(II) complexes is shown to be upto 180 . Then some weight started losing upto 315 C, may be due to liberation of gas molecules like Cl2, NO2, etc. The horizontal platev in the temperature range 220-380 C clearly show the thermal stability of the complexes. The heavy loss in weight between 430-640 C indicate the decomposition of coordination sphere to form CO2, H2O, and ultimately U3O8 uranium sesqui-oxide, which is most stable oxide of uranium.

DTA curves of the complexes show endothermal peaks at 230 and 460 (complex I) and 210 and 440 C complex (II) and 210 and 410 C complex (III) respectively, where as exothermic peaks are observed at around 400 ; 460 ; 520 (1); 400, 470, 500 C (II) and 400, 520, 540 (III) shows the decomposition of organic part with the formation of U3O8. Schematically representation of Pyrolytic behaviour of uranyl complexes given below:-

1. [UO2 (C11H13N3O3S)2] (CH3COO)2 $\xrightarrow{40-170°C}$ [UO2(C11H13N3O3S)2]

(CH3COO)2 $\xrightarrow[-(CH3COO)2]{170-300}$ UO2(C11H13N3O3S)2 $\xrightarrow[- 2L]{330-620°C}$ UO3 $\xrightarrow{[O]}$ U3O8.

2. [UO2 (C11H13N3O3S)2](NO3)2 $\xrightarrow{40-170°C}$ [UO2 (C11H13N3O3S)2](NO3)2

$\xrightarrow[- 2NO3]{170-300}$ UO2(C11H13N3O3S)2 $\xrightarrow[- 2L]{330-620°C}$ UO3 $\xrightarrow{[O]}$ U3O8

3. [(UO2)2 (C19H19N3O4S)2](NO3)4 $\xrightarrow{40-170°C}$ [(UO2)2(C19H19N3O4S)2]

(NO3)4 $\xrightarrow{170-300°C}$ [(UO2)2(C19H19N3O4S)2] $\xrightarrow{330-620°C}$ UO3 $\xrightarrow{[O]}$ U3O8

The complexes exhibit high thermal stability and get decomposes only above 180 C, indicating absence of absorbed

moisture or lattice water(46). Exothermic peak at higher temperature may be due to decomposition of the organic ligand and subsequent slow oxidation(47).

Infra red spectral studies:-

(i) Cu(II) complexes- [Cu (C11H13N3O3S)3] Cl2 and [Cu (C11H13N3O3S)2] Cl2 The coordination sites of the ligand involved in coordination with metal ion have been as certained by comparing the spectra of the complexes with parent compounds. Some important frequencies diagnostic of chelation with the metal ion have been discussed here. Phenyl glyoxal thiosemicarbazone show intense absorptions at 3400, 1635, 1350, 1690 and 810 cm -1 which may respectively assigned to (NH) stretch, γ(C=N) and γ(N-H) bonding, γ(C=S) + γ(C-N) > C=O, and γ(C=S), the corresponding bands are observed in the spectra of Cu complex at 1600 cm -1 and 1630 cm -1. Thus the negative shift in (CH=N) and > C=O suggest coordination through the azomethine nitrogen(48-49) and ketonic oxygen. Further the band at 810 cm -1 due to > C=S remain unaltered in chelation suggesting non participation of Thiol group.

Therefore phenyl glyoxal thiosemicarbazone seems to behave as bidentate ligand and the coordinationg sites are azomethine nitrogen and ketonic oxygen atoms. Lowering in the frequencies of -CH=N and > C=O are due to the drainage of electron. from Nitrogen and oxygen atom in chelation, which in turn weaken the bonds.

The non ligand bands appearing in far IR region in the spectra of the complexes, have been assigned to γ(M-O) and γ(M-N) modes(50-51).

Table (5.9) IR spectral assignments of Cu (II) complexes of (C11 H13 N3 O3 S) and (C19 H19 N3 O4 S)   page no. 103

S.No.	Compounds	NH-stretch	ν(C=N) and N-H Bending in plane	(C-H) Benzene	ν(C=S)+ ν(CN)	νC=O	ν(C=S)	(NH) out of plane	ν(M-N) / ν(M-O) / ν(M-S)
1	(C11 H13 N3 O3 S)	3410 ms 3300 m 3210 m	1640 m	1410 (m) 1460 (m)	1360 vs	1680 s	800 s 1220 m	680 m	-
2	(C19 H19 N3 O4 S)	3340 (m) 3400 (ms) 3220 (m)	1630 m	1410 (m) 1460 (M)	1370 vs	1690 s	805 s 1210 m	675 m	-
3	[Cu (C11 H13 N3 O3 S)3]Cl2	3410 ms	1610 w	1400 m	1350 vs	1620 w	810 s 1200 m	675 m	360m/410m
4	[Cu(C11 H13 N3 O3 S)2]Cl2	3390 m	1600 (w)	1410 m	1360 vs	1630 w	800 s 1210 m	680 m	370w/430m
5	[Cu2(C19 H19 N3 O4 S)2]Cl4	3360 (m)	1605 (vs)	1390 m	1340 vs	1630 w	780 (s) 1170 (m)	700 m	400w/430m

Table (5.10) IR spectral assignments of mn (II) complexes of (C11 H13 N3 O3 S) and (C19 H19 N3 O4 S)

S.No.	Compounds	NH-stretch	ν(C=N)and N-H Bending	(C-H) Benzene in plane	ν(C=S)+ ν(CN)	ν C=O	ν(C=S)	(NH)out of plane	ν(M-N) ν(M-O) ν(M-S)
1	(C11 H13 N3 O3 S)	3405 ms 3300 m 3210 m	1640 m	1410 (m) 1460 (m)	1360 vs	1680 s	810 s 1220 m	680 m	—
2	(C19 H19 N3 O4 S)	3360 (m) 3410 (ms) 3220 (m)	1645 m	1410 (m) 1450 (m)	1370 vs	1690 s	805 s 1280 m	670 m	—
3	[mn (C11 H13 N3 O3 S)2 C12]	3330 m 3410 m	1610 w	1390 m 1420 m	1350 vs	1660 w	800 w 1280 m	670 m	500m/460w
4	[mn(C11 H13 N3 O3 S)2(NH3)2]	3330 m	1610 w	1390 m 1430 m	1360 vs	1680 (w)	800 s 1280 m	670 m	500w/450w
5	[mn2(C19 H19 N3 O4 S)2 C14]	3330 m	1600 m	1405 m	1320 vs	1640 m	760 w 1200 m	660 m	500w/450m /400w

Table (5.11) IR spectral assignments of Uranyl complexes of (C11 H13 N3 O3 S) and (C19 H19 N3 O4 S)   page no. 105

S.No.	Compounds	NH-stretch	ν(C=N) and N-H Bending	(C-H) Benzene in plane	ν(C=S)+ ν(CN)	ν C=O	ν(C=S)	(NH) out of plane	ν(M-N)	ν(M-O)	ν(M-S)
1	(C11 H13 N3 O3 S)	3400 ms 3290 m 3200 m	1635 m	1400 (m) 1450 (m)	1350 vs	1690 s	810 s 1220 m	680 m	—		
2	(C19 H19 N3 O4 S)	3350 m 3400 ms 3210 m	1635 m	1400 (m) 1450 (m)	1360 vs	1700 s	805 s 1220 m	670 m	—		
3	[UO2(C11 H13 N3 O3 S)2] (CH3COO)2	3400 (w) 3410 m	1570 w	1380 (m)	1340 m	1600 w	810 w 1220 m	640 m			480m/410m
4	[UO2(C11 H13 N3 O3 S)2](NO3)2	3370 w	1575 w	1380 w	1280 s	1630 m	760 m 1330 w	640 m			460w/440w
5	[(UO2)2(C19 H19 N3 O4 S)2(NO3)4	3370 w	1570 w	1400 w	1280 s	1630 m	760 m 1180 w	640 m			460w/440w /400m

Wave Length (Microns)

$[Cu(C_{11}H_{13}N_3O_3S)_3]Cl_2$

$[Cu(C_{11}H_{13}N_3O_3S)_2]Cl_2$

$[Cu_2(C_{19}H_{19}N_3O_6S)_2]Cl_4$

Transmittance (%)

Wave number (cm^{-1})
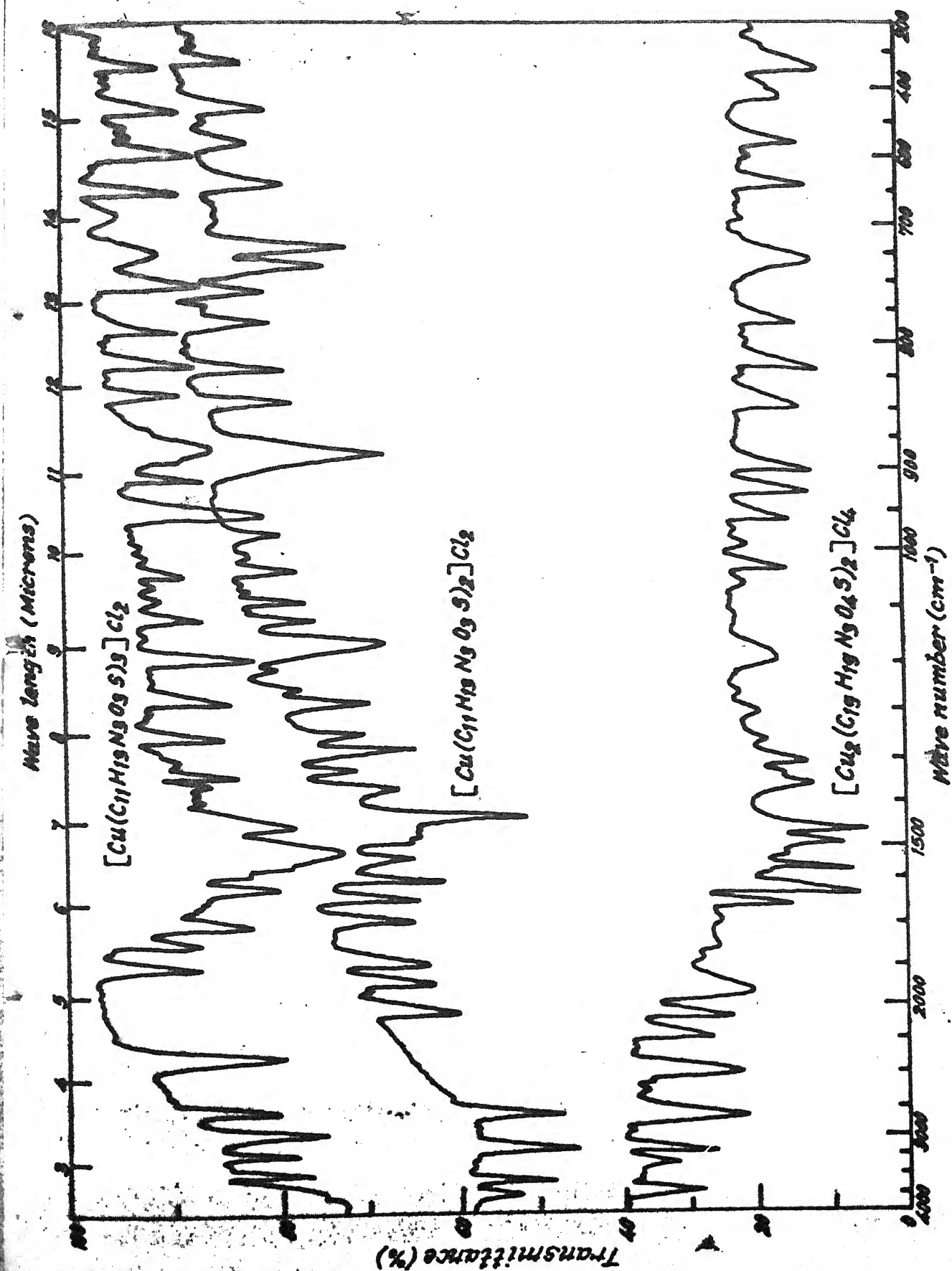
Fig. (5.1): I.R. Spectra of Cu(II) complexes.

(ii) [Cu2 (C19H19N3O4S)2] Cl4 — 4-p- methoxy phenyl thiosemicarbazone of phenyl glyoxal behave as Tetradentate ligand, and the coordinating sites are >C=O, —CH=N, >C=S and —CH=N. A sharp band at 1630 cm —1 (CH=N) of the compound indicate the coordination because this frequency considerable reduces on complexation(52-53). The sharp to medium broad absorption bands observed in the region 3200-3400 cm —1 due to (NH) remain unaltered in complex spectra. A single >C=O band observed at 1700 cm —1 in the spectra of the ligand suffered a negative shift of 60 cm —1 in the spectra of the complex, indicating coordination, through ketonic oxygen atom. Satapathy and Sahoo(54) reported two (C=N) bands at 1613 and 1595 cm —1 in case of Fe(II) complex but we observed one band at 1600 cm —1 which suggest coordination of both the (CH=N) group. The coordination through both the azomethine group is further supported by shifting in the frequency of (N-N) in complexes(55).

The band appearing at 1220 and 815 cm—1 assigned to (C=S) stretching vibration is susceptible to coordination. In metal complex it shifts to lower frequency at 1170 cm —1 showing coordination of sulphur atom with metal(56).

Other bands noticed in the spectra of ligands at 700, 740 cm —1 shift in an irregular way in the metal complexes, which probably arises due to out of plane CH-bending absorption of the benzene ring(57).

Absorption observed in the far infra red regions have been assigned to $\sqrt{}$(M-O) 490 cm —1, $\sqrt{}$(M-N) 500 cm —1 and 400 cm —1 $\sqrt{}$(M-S) bonds. Such assignments have also been reported by earlier workers(58).

In some cases high frequencies for (M-S) may also be expected(59).

The (NH3) stretching frequency observed at 3205 and 3140 cm -1 can be assigned to symmetrical stretching vibrations of NH3 molecule.

Thus on the basis of IR studies it may be concluded that the ligand act as tetradentate and the coordinating sites are two azomethine group, one>C=O and one C=S group.

Manganese (II) complexes:- [Mn (C11H13N3O3S)2 Cl2]; [Mn (C11H13N3O3S)2 (NH3)2] [Mn (C19H19N3O4S)2 Cl4] The tentative assignments for IR absorption bands in the range (4000-400 cm-1) for Mn(II) complexes are based on the corresponding compounds (60-62).

In (C9H9N3OS)-Mn(II) complexes the sharp band at 1635 cm-1 (-CH=N) shifts to lower frequencies at ~ 1600 cm-1 in the complexes showing the coordination through nitrogen atom, similar observations are reported earlier(63).

Further a band at 1690 cm-1 due to >C=O is shifted downward in their complexes by 20-30 cm-1 indicating that the oxygen atom of ketonic group involved in coordination.

The bands at 1280 and 810 cm-1 in free ligand are probably due to $\sqrt{}$(C=S). Besides these bands a week band 2500 cm-1 due to (SH) is also noticed in the spectra of free ligand. This is probably due to the presence of Thioenolic form in the ligand which on complexation does not shift either upward or down ward, showing it does not take part in chelation(64).

In (C19H19N3O4S) -Mn(II) complexes the band at 1635, 1360; 1700; 805(1280) have been assigned to $\sqrt{}$(C=N); $\sqrt{}$(C=S+CN);
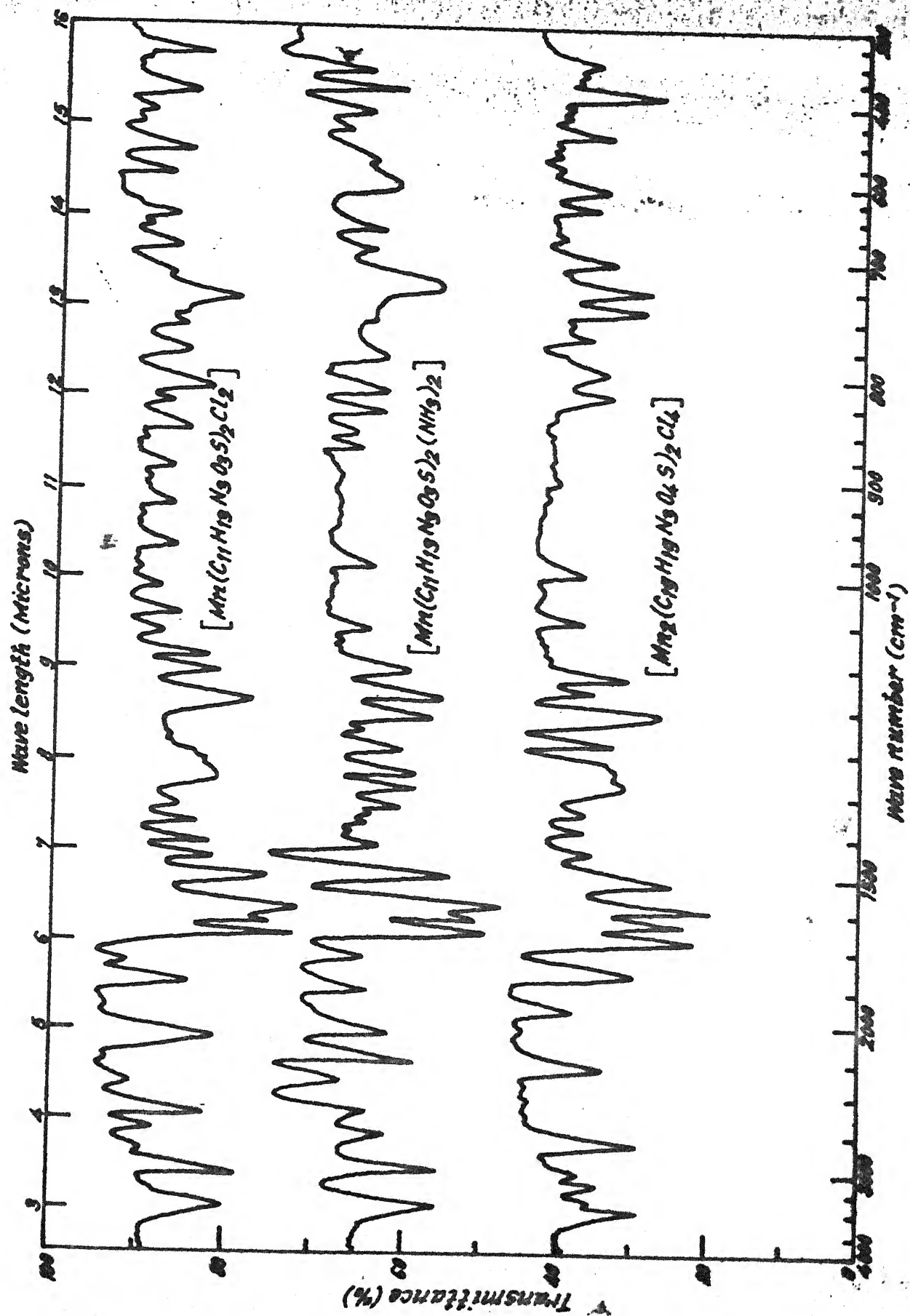
Fig.(5.2): I.R. Spectra of Mn(II) complexes.

$> C=O$ and $> C=S$ grouping on complexation the frequencies of $>C=O$, $-CH=N$ and $> C=S$ grouping changes considerably. It is observed that coordination of sulphur considerably lower (C=S) stretching frequency due to the drainage of electrons from the sulpher in chelation which in turn weaken the (C=S) band(66-67), suggest coordination of the metal ion through sulphur atom of the $>C=S$ group.

All the ligands show two ν(N-H) bands at 3400 and 670 cm-1 which do not undergo any appreciable shift on complex formation, indicating non coordination of (NH2) group.

In the far infra red region, the complex show new bands located in the range 480-400 cm-1 are tentatively assigned to γ(M-N) and ν(M-S) stretching vibrations(68-70).

Brown and Kubota(71) reported different regions of ν(M-X), where X=Cl/Br, depending upon the stereochemistry around coordinated metal ion. In octahedral and tetrahedral complexes ν(M-Cl), frequency found around 250-200 cm-1 and 350-280 cm-1 as reported in literature(72-73). It is observed (74-75) that the complexes having only one coordinated halogen the stretching frequencies (M-Cl) are intermediate between those found in tetrahedral and octahedral complexes. The complexes show one weak broad band at about 400 cm-1 which is assigned to (M-Cl) bonds.

Uranyl Complexes- [UO2(C11H13N3O3S)2] (CH3COO)2;

[UO2(C11H13N3O3S)2] (NO3)2; [UO2(C19H19N3O4S)2] (NO3)4 On comparing the spectra of free ligands and the complexes, considerably reduction in the frequencies of $>C=O$, $-CH=N$; and
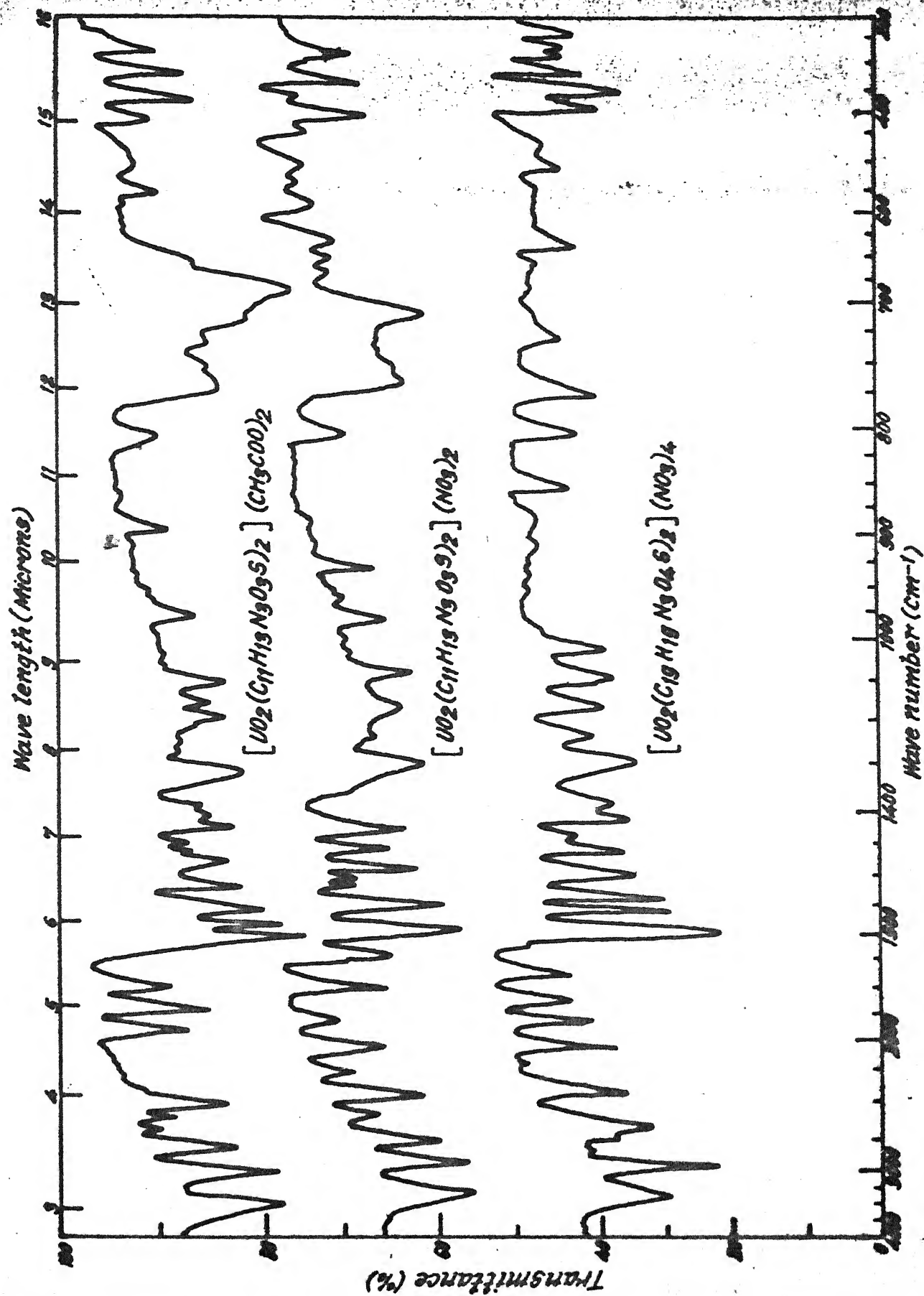
Fig. (5.3) : I.R. Spectra of Uranyl complexes.

>C=S have been noticed. This show these are the active sites of participation in complexation(76-77). Further the directions of the shift in the positions of all the bands in the spectra of the complexes are same, suggesting similar stoichiometry.

New bands appears in the far infrared region inthe spectra of the complexes, assigned to ν(M-N); ν(M-O) and ν(M-S) vibrations(78).

CHAPTER-V

REFERENCES

1.   O. Kahn —Inorg. Chim Acta 62 (1982)3.

2.   S.L. Lambert, C.L. Spiro, R.P. Gagne and D.N. Hendriskson — Inorg. Chem. 21(1982)68.

3.   M. Nakamura, H. Okawa and M. Nonoyma — Inorg. Chim. Acta 62 (1982)201.

4.   K. Nonoyama, H. Ojima and S.Kida — Inorg. Chim. Acta 59(1982) 275.

5.   R.J. Butcher. J.O. Corner and E. Sinn — Inorg. Chem. 20(1981) 3486.

6.   B.C. Whitmore and R.Eisenberg — Inorg. Chim. 22 (f1983)1.

7.   M. Keeton, A.B.P. Lever and B.S. Ramaswamy — Can. J. Chem. 48, 3185 (1970).

8.   M. Nonoyama — Inorg. Chim. Acta 10, 59 (1974).

9.   B.J. Hathaway and D.E. Billing — Coord. chem. Rev. 5, 143 (1970).

10.   M. Kato, H.B. Jonassen, and J.C. Fanning — Chem. Rev. 64, 99, (1964).

11.(a) S. Yamada — Chem. Abst. 73, 8332 g (1970).

   (b) K.S. Arulsamy, R.F.N. Ashok and U.C. Agarwal — Ind. Jour of Chem. 23A (1984)21.

12.   A.T. Phillip, W. Mazurek and A.T. Casey — Aust. J. Chem. 24, 501 (1971).

13.   F. Lions, I.G. Dance and J. Lewis — J. Chem. Soc(A) 565 (1967).

14.   D.P. Madden and S.M. Nelson — J. Chem. Soc. (A) 2342(1968).

15.   M.   Ciampolini and M.   Nardi — Inorg.   Chem.   5, 41, 45, 1150(1966).

16.   M. Nakamura, H. Okawa and S. Kida — Inorg. Chim. Acta 62 (1982) 201.

17.   S.B.   Saxena and Y.K.   Agarwal — J.   Ind.   Chem. Soc. 57 (1985) 279.

18.   D.E.   Fenton,   U.   Casellato P.A. Vigato and M. Vidali — Inorg. Chim. Acta 62 (1982) 57.

19.   G.A.   Nicholson,   J.L.   Peterson   — Inorg.   Chem. 9(1980)2198.

20.   R.L.   Dutta   and   Md.   Munkir Hossain   — Ind.   J.   Chem. 23A(1984) 30.

21.   M.H.   Sonar and A.S.   Murty — J.   Inorg.   Nucl. Chem. 42 (1980) 815.

22.   A.P.B.   Lever   — Inorganic.   Electronic   Spectroscopy- (Elsevier, Eastern, New Delhi) 1972,916.

23.   M.R. Udupa and K.S. Nagrja —Thermo Chim. Acta 56(1982)241

24.   Y. Bishida and S. Kida — Coord. Chem. Rev. (1979), 27.275

25.   N.V. Huggi, M.B. Halli and A.C. Hiremath — J. Ind. Chem. Soc, 59 (1982)1017.

26.   P.C. Nigam and R.D. Srivastava — Ind. J. Chem.19A (1980) 563.

27.   P.C. Nigam, Madhuphull and H.C. Bajaj — Talanta 28(1981). 610.

28.   P.K. Biswas and N. Ray Chaudhri —Ind. Jour.of Chem. 23 A (1984) 109.

29.   P.K.Biswas and N.Ray Chaudhri—J chem Soc.   Dalton Trans (1981) 2385

30.   D.Hibdon and J.H.Nelson - Inorg. chem Acta (1973), 7, 629

31.   R.C.Agarwal Seema Agarwal and N.K.Singh - Ind. Jour of
        chem. 23 A (1984) 137

32.   C.Belin, M.Chaobouni, J.L.Pascal. J.Potier and J.Roziere-
        chem. Commcum (1980) 105.

33.   Carlopreti and G.Toshai - J. Coord. Chem . Vol.6 (1978)
        15.

34.   Sunil Kumar, R.K.Mahajan and V.P.Kapila - Ind-J. chem 22A
        (1983) 490.

35.   A.Earnshaw, M.Meidt and B.Ewald -J. chem. Soc.(1966) 1658

36.   R.A.Bhobe -J. Ind.chem Soc. 52, 390 (1975); 344 (1977).

37.   L.Doretti, S.Sitran, F.Madalosso, G.Banddi and
        G.Paolucci - Jour. Inorg. nucl. chem. 42 (1980) 1060.

38.   H.H.Jaffe and M.Orchin "Theory and application of
        ultraviolet Spectroscopy" - John. Wiley N.Y. (1964).

39.   S.P.Mc Glynn and J.K.Smith - J.Mol. Spectroscopy -
        (1961),6, 164.

40.   M.M.Jones,- J. Chem. Phys.(1955). 23 , 2105; A.E.Comyns,
        B.M. Gate house and E. Watt - J. chem. Soc.(1958), 4655.

41.   A.Syamal and O.P. Singhal - Transition metal chem. (1979)
        4, 179.

42.   J.Lewis and M.Schroder - J.Chem. Soc. Dalton Trans (1982)
        1085.

43.   Coordination chemistry of macrocyclic compounds - edited
        by G.A.Melson (Plenum Press, New York) 1980.

44.   C.A.Jopsen and J.E House (Jr) -J. Inorg Nucl. chem. 43
        (1981) 953.

45.   J.Singh and N.K.Singh — Ind. J.chem. 21 A (1982) 536.

46.   A.V.Nikolaev, V.A.Lagvienko and L.I.Mayachina — Thermal Analysis Vol.2, (Academic press, New York) 1969 , 779.

47.   N.S>Bhave and R.B.Kharat — J. Ind. chem. Soc. 58(1981) 1194.

48.   K.Nagano, H.Kinoshita and A.Hirakawa — Chem. Pharm. Bull. (1964), 12 1198.

49.   C.N.R.Rao "Chemical application of infrared spectroscopy" — Academic press New York. (1964) pp. 758-765.

50.   J.L.charpantier and T.Moeller — J. Inorg. Nucl. Chem. (1970) 32, 3575.

51.   N.Ngsee, H.W.Latz and D.G.Hendricker — J. Inorg . nucl. Chem. (1977), 39, 71.

52.   W.Henke and S.Kramer — Inorg chem. Acta 65 (1982) L 115.

53.   R.C.Sexana, C.L.Jain and H.S.Verma — Ind. J.Chem. 16 A (1978) 167.

54.   S.Satapathy and B.Sahoo — J. Inorg. Nucl. Chem. (1970) 32. 2223.

55.   A.Braibanti, F.dallavale, M.A.Pellinghelli and E.Leoporati. Inorg. chem. (1968) 7, 1430.

56.   K.C.Satpathy, H.P.Mishra and T.D.Mahana — J. Ind. chem. Soc. (1979), 56, 248.

57.   L.J.Bellamy —"Infra red spectra of complex molecules" — Methuen and Co. ltd. london. ec. 4, (1968) 82.

58.   K.Nakamoto —Infra red spectra of inorganic and coordination compounds (Wiley , New York) 1983, 77.

59.   Y.Thakur, J.Thakur and A.K.Singh — J. Ind. Chem. Soc. (1979) 56.

60.   A.Syamal and O.P.Singhal - J. Inorg. Nucl. Chem. 43
        (1981) 2821.

61.   R.C.Sharma and M.K.Rastogi Ind.   Jour.   of Chem.
        23A(1984) 431.

62.   M.J.M.Campbell, A.J.Collins and R.rzeskowiak - Jour.
        Inorg. Nucl. Chem. 18 91976) 173.

63.   D.V.Raman Rao and B.Pardhan - J. ind. Chem. soc. 54, 136
        (1977).

64.   K.C.Satpathy and T.D.Mahana - J. ind. chem. soc. 56(1979)
        1173.

65.   M.J.M.Campbell and R.Grazeskowiak - J. Chem soc. (A)
        (1967) 396.

66.   H.S.Melhotra and R.K.ultani:- Ind. Jour. of Chem. (1984)
        23 A , 434.

67.   D.V.Raman Rao and B. Pardhan - J. Ind. chem. Soc. 48, 136
        (1971).

68.   K.S.Siddiqi, N.H.Khan and S.A.A.Zaidi etal- Ind. Jour of
        Chem. 26A (1987) 492.

69.   M.Akbar ali, S.E.Livingstone and D.J. Phillips - inorg.
        Chem. Acta (1971) 5, 119, 493.

70.   Y.D.Kulkarni, Nisi Saxena and O.P.Srivastava- Ind. Jour
        of chem. 29A (1990) 77.

71.   S.L.Chadha and Kamini Uppal- Ind.Jour of Chem.29A(1990)80

72.   R.C.Mehrotra, D.C.Bragley and D.P.Gaur- Metal Alkoxides
        (Academic press) London (1972).

73.   M.Gold stein and W.D. Unsworth - Inorg. Chem. Acta 4
        (1970) 342.

74.   M.Akbar Ali and D.J.Philips — Jour Inorg. nucl. chem. 36 (1974) 2229.

75.   S.L.Chadha and V.z. Sharma — Z. anorg. allg. chem. 545(1987) 227.

76.   K.S.Siddiqi and A.S.S. Zaidi etal— Ind. jour of Chem. 29A (1990)82.

77.   Chem. Diew and A.E.Mardell Inorg. chem. 26 (1987)1026.

78.   B.S.Reddy— Ind. Jour of Chem. 29A (1990)86.

Chapter-VI

Magnetic and spectroscopic studies on cubic high spin Ni (II) and Co (II) complexes with O,N,S donors.

Introduction:- The transition metal Schiff base chelates derived from tetradentate or bidentate Schiff bases have been extensively studied (1-2). Some square planar complexes of C4V symmetry have been discussed in recent years. (3) The composition protonation constants of Schiff bases (4) complexes of Ni (II), Co (II) have been determined by Irving Rossotti method (58).

Nickel (II) complexes have been found to exist both in low and high spin states confirming to trigonal bi-pyramidal and square pyramidal geometries. Square pyramidal nickel (II) complexes with 3 B1 ground level are expected to produce a spin only value for magnetic moment. However this level is mixed with the excited E- levels, through spin orbit coupling. Detail of spin orbit coupling has been dealt by Gerloch etal; (6) to account for the magnetic properties of square pyramidal complexes.

A number of complexes have been reported with O-aminobenzoic acid which exhibits diverse type of coordination with different metal ions (7). Mehrotra and Coworkers (8) have extensively studied the reactions of alkoxides of titanium (IV) and zirconium (IV) with salicylaldehyde Effects of different anions on the structure of some mixed ligands complexes of transition metal ions with various amines have been reported by Shukla etal (9).

In this chapter it is proposed to calculate different ligands field parameters using Konig equations of Octahedrally

1

coordinated as well as square planar transition metal complexes of Ni (II) d8 and Co (II) d7 with Schiff base type ligands namely 2.5 Dimethoxy Phenyl-glyoxal thiosemicarbazone and 4-p-methoxy phenyl thio-semicarbazone of 2.5 Dimethoxy Phenyl glyoxal obtained through the condensation of 2.5 Dimethoxy Phenyl glyoxal and thiosemicarbazone.

EXPERIMENTAL

Preparation and Isolation of nickel (II) complexes:-

1.   [Ni ($C_{11} H_{13} N_3 O_3 S$)] Cl_2 — ABrown coloured mass was obtained after refluxing $NiCl_2$. 6 H_2O (1.18 g. 0.05 M) and 2.5 Dimethoxy Phenyl glyoxal thisemicarbazone 0.01 M (1:1) over steam bath , after cooling Solid brown coloured compound separated out. It was filtered washed and dried under vacuum over fused anhydroys $CaCl_2$.

2.   [Ni ($C_{11} H_{13} N_3 O_3 S$)2 (NH_3)2] Cl_2 — To a 1.1 ethanolic solution of ligands and nickel chloride was added few ml of liquor ammonia to raise the ph ~ 6.5 of the mixture. The content was refluxed for 1-2 hours when yellowish green mass was obtained. It was collected on buchner funnel, and then washed, dried over P_4O_{10}.

3.   [Ni ($C_{11} H_{13} N_3 O_3 S$)2 (NO_3)2]— It was prepared by reacting an ethanolic solution of Ni (NO_3)2. 6 H_2O and the ligands in 1:2 stoichiometrie ratio, after refluxation for about an hour greenish coloured mass appeared . It was filtered washed with ethanol and dried in vacuo.

4. $[Ni(C_{11}H_{13}N_3O_3S)_2(H_2O)_2]SO_4$ - It was prepaed (brown colour) by mixing ethanolic solution of $NiSO_4.7H_2O$ and the ligand in stoichiometric ratio (1:2) after refluxation for about an hour. The adduct was filtered, washed and then dried in air oven at 80 C.

5. $[Ni_2(C_{11}H_{19}N_3O_4S)_2]cl_4$ - Dark brown coloured mass was obtained by reacting ethanolic solution of $NiCl_2.6H_2O$ and 4-p-methoxy phenyl-thiosemicarbazone of 2.5 Dimethoxy phenyl glyoxal in required stoichiometric amount 1:2. After refluxation and cooling, coloured mass was filtered, washed and dried in air oven at 80 C.

Cobalt (II) complexes

1. $[Co(C_{11}H_{13}N_3O_3S)_3]Cl_2$- The brownish blue coloured precipitate was obtained by reacting $CoCl_2.6H_2O$ and 2.5 Dimethoxy phenyl glyoxal thiosemicarbazone dissolved in ethanol in 1:3 stoichiometric ratio. It was digested on water bath for nearly one hour, and cooled, gave brownish blue mass. It was filtered, washed with water and dried.

2. $[Co(C_{11}H_{13}N_3O_3S)_3]_2H_2O$ -- To the above prepared complex dissolved in ethanol, few ml of liquor ammonia was added to raise the pH~ 6.5, when violet brown colour mass was obtained, after refluxing the contents for about an hour. It was filtered washed and dried.

3. $[CO(C_{11}H_{13}N_3O_3S)_3](NO_3)_2$ - By following the above procedure dark brown coloured precipitate was obtained. It was treated and collected in the usual manner.

4.   [Co (C19 H19 N3 O4 S) Cl2] – Bluish green coloured compound was prepared by mixing CoCl2. 6 H2O (1.18 g, 0.005 M) dissolved on ethanol and 4-p-methoxy phenyl thio-semicarbazone of 2.5 Dimethoxy phenyl glyoxal in the same solvent in 1:1 stoichiometry. Contents were refluxed for about an hours, giving the required compound, It was filtered, washed with water. ethanol and dried in air oven at 80 C.

5.   [Co (C19 H19 N3 O4 S)(NH3)2]– Ammonia derivative was obtained by adding ethanolic liquor ammonia to the above compound, by maintaining the pH~ 6.5. After raising th pH it was refluxed for about an hour, filtered, washed with water, ethanol and dried air oven at 80 C.

6.   [Co (C19 H19 N3 O4 S) (CH3 COO)2]–It was prepared by heating and then digesting the mixture containing ligands (0.005mol) and cobalt acetate diyhdrate (0.005M). On water bath. It was filtered washed with ethanol and dried.

7.   [Co2 (C19 H19 N3 O4 S)2 Cl4] H2O –The greenish solid metal chelate was synthesised by refluxing a mixture of cobalt chloride hexahydrate (0,01 M in 10-15 Ml ethanol) and the ligand (0.01 M in the same volume) for 2 hour on water bath. On concentrating the mixture the coloured mass obtained was filtered, washed with ethanol and dried. .

Results **and** **discussion:–** Analytical, magnetic, electronic spectral data and IR are represented in tabular forms.

Nickel **(II)** **complexes** – The magnetic moment value for [Ni(C11 H13 N3 O3 S)] Cl2 (0.28 B.M.) points towards diamagnetic

character of the complexes with square planar stereochemistry of the ligand around nickel (II), ion while other Nickel (II) complexes,namely $[Ni (C_{11} H_{13} N_3 O_3 S)_2 (NH_3)_2] Cl_2$ (2.94 B.M.) $[Ni (C_{11} H_{13} N_3 O_3 S)_2 (NO_3)_2]$ (3.00 B.M) $[Ni (C_{11} H_{13} N_3 O_3 S)_2 (H_2O)_2 SO_4;$ (3.52 B.M.) and $[Ni_2 (C_{19} H_{19} N_3 O_4 S)_2)] Cl_4$ (3.24 B.M) corresponding to two unpaired electrons, revealing[10-12] high spin octahedral stereochemistry around[13] Ni (II) ions. Magnetic moment values are in fairly good agreement with the values calculated by substituting the expeimental quantities,

Table (6.1) Analytical and magnetic date of Ni (II) Complexes.

S.No.	Compound	Chemical analysis calcd/ (Found) Anion						Magnetic Data		Stereo chemistry
		C	H	N	S	Cl	Metal	X 1 mx 10⁻⁶ Cgsu	µeff (B.M)	
1	[Ni (C 11 H13 N3 O3 S)2] cl2	39.77 (38.90)	3.91 (3.11)	12.65 (12.19)	9.64 (8.60)	10.69 (10.00)	8.84 (7.64)	32.70	0.28	Square Planar
2	[Ni(C11 H13 N3 O3 S)2 (NH3)2] cL2	37.83 (37.02)	4.58 (4.08)	16.05 (15.12)	9.17 (8.90)	10.17 (9.10)	8.41 (8.00)	3622.8	2.94	H.S.O.
3	[Ni(C11 H13 N3 O3 S)2 (NO3)2]	36.83 (36.02)	3.62 (3.30)	15.62 (14.65)	8.92 (8.34)	-- --	8.19 (7.85)	3772.23	3	H.S.O.
4	[Ni(C11 H13 N3 O3 S)2(H2O)2]SO4	36.42 (35.63)	4.13 (3.98)	11.59 (10.76)	13.24 (12.40)	-- --	8.10 (7.60)	5193.55	3.52	H.S.O.
5	[NI2(C19 H19 N3 O4 S)2] cl4	44.29 (43.74)	3.69 (3.18)	8.15 (8.08)	6.21 (5.85)	13.79 (12.80)	11.40 (10.86)	4400.14	3.24	H.S.O.

H.S.O. -- High spin octahedral

Table (6.2) Analytical and magnetic date of Cobalt (II) Complexes.

S.No.	Compound	Chemical analysis calcd/(Found)						Magnetic Data		
		C	H	N	S (Anion)	Cl	Metal	X 1 mx -6 10 Cgs Unit	µeff (B.M)	Stereo chemistry
1	[Co (C 11 H13 N3 O3 S)3] cl2	42.53 (41.76)	4.18 (3.84)	13.33 (12.35)	10.31 (9.82)	7.62 (7.20)	6.32 (5.68)	9577.10	4.78	H.S.O.
2	[Co (C11 H13 N3 O3 S)3 2H2O	44.20 (43.13)	4.79 (4.10)	14.06 (13.33)	10.71 (9.88)	--	6.57 (6.11)	9819.3	4.84	H.S.O.
3	[Co (C11 H13 N3 O3 S)3](NO3)2	40.24 (39.83)	3.96 (3.72)	15.65 (14.27)	9.75 (8.80)	--	5.98 (5.15)	10988.2	5.12	H.S.O.
4	[Co (C19 H19 N3 O4 S)cl2]	44.27 (44.00)	3.68 (3.12)	8.15 (7.55)	6.21 (5.90)	13.78 (12.45)	11.44 (10.72)	10563.0	5.02	H.S.O.
5	[Co(C19 H19 N3 O4 S)(NH3)2]	47.70 (47.10)	5.23 (4.94)	14.64 (13.83)	6.69 (5.30)	--	12.32 (11.75)	10270.4	4.95	H.S.O.
6	[Co(C19 H19 N3 O4 S)(CH3COO)2]	49.11 (48.92)	4.44 (3.89)	7.49 (6.42)	5.69 (5.12)	--	10.48 (9.59)	10647.3	5.04	H.S.O.
7	[Co2(C19 H19 N3 O4 S)2cl4]H2O	43.51 (43.16)	3.81 (3.18)	8.01 (7.17)	6.10 (5.75)	13.55 (12.12)	12.70 (12.16)	11334.1	5.2	H.S.O.

High spin octahedral --- H.S.O

Table (6.3) Eectronic spectral data and calculated transition energies cm-1 of the spin

allowed bands in Octahedral Ni (II) complexes

S.No.	Compound	Method Calculation	Observed and calculated Transition energies 3 A2g (F)----->			B 35 cm-1	β35	δv cm-1	δvx	LFSE Kcal/mole
			3T 2g (F)	3T 1g (F)	3T 1g (ρ)					
1	CNi (H2O) 6]++	Expt.	8500	13800	25300	-	-	-	-	-
		(a) 10 Dg		Fitted	24005	753.8	0.72	-2293	-	-
		(b) 10 Dg		14144	Fitted	929.6	0.89	+344	-	-
		(c) 10 Dg		14108	24993	906.3	0.87	+307	-	-
		(d) 10 Dg		14187	25687	958.3	0.92	+387	-	-
2	CNi (C11 H13 N3 O3 S)2 (NH3)2]cl2	Expt.	10000;12200	16400	28040	-	-	-	-	
		(a) 10 dg		Fitted	29111	960	0.922	+1071	3.8	34.28
		(b) 10 dg		16420	Fitted	963	0.925	+20	0.12	
		(c) 10 dg		16405	28020	962	0.925	-20	0.07	
		(d) 10 dg		16412	28030	963	0.925	±10	0.03	
3	CNi(C11 H13 N3 O3 S)2 (NO3)2]	Expt.	9325;12000	14780	27530	-	-	-	-	
		(a) 10 dg		Fitted	23722	702	0.675	-3808	13.83	31.95
		(b) 10 dg		15477	Fitted	1003	0.964	+697	4.71	
		(c) 10 dg		15410	26891	955	0.918	+639	2.32	
		(d) 10 dg		15580	28320	1062	1.02	+800	5.41	

Table (6.4) Eectronic spectral data and calculated transition energies (cm-1) of the spin

allowed bands in Octahedral Ni (II) complexes

S.No.	Compound	Method Calculation	Observed and calculated Transition energies -----> 3 A2g (F)----> 3T 2g (F);	3T 1g (F)>3T 1g (p);		B 35 cm-1	β35	δν cm-1	δν%	LFSE Kcal/ mole
4	[Ni(C 11 H13 N3 O3 S)2 (H2O)]SO4	Expt.	9400;12080	14880	27000	-	-	-	-	-
		(a) 10 Dg		Fitted	23830	701	0.672	-3170	11.74	32.22
		(b) 10 Dg		15520	Fitted	954	0.917	+640	4.3	
		(c) 10 Dg		15444	26440	912	0.876	+560	3.76	
		(d) 10 Dg		15600	27603	1009	0.97	+720	4.83	
5	[Ni (C19 H19 N3 O4 S)2]Cl4	Expt.	9200;12300	14700	27600	-	-	-	-	
		(a) 10 dg		Fitted	23780	729	0.7	-3820	13.84	31.54
		(b) 10 dg		15328	Fitted	1022	0.982	+628	4.27	
		(c) 10 dg		15270	27033	980	0.942	+567	2.05	
		(d) 10 dg		15570	28201	1074	1.032	+810	5.5	

Table (6.5) Relevant ligand field and 'NSH' Energy parameters for Ni (II) octahedral complexes.

S.No.	Parameter	[Ni (C11 H13 N3-O3 S)2 (NH3)2]cl2	[Ni (C11 H13 N3-O3 S)2 (NO3)2]	[Ni (C11 H13 N3-O3 S)2 (H2O)2]SO4	[Ni (C19 H19 N3-O4 S)2]cl4
1	B-Value from ν/cm	960	702	701	729
2	V2/V1	1.64	1.58	1.58	1.59
3	V3/V2	1.70	1.86	1.81	1.86
4	C--Cm-1	3840	2808	2804	2916
5	F 2 cm-1	20160	14742	14770	15309
6	F 4 cm-1	48384	35380.8	35330.4	36741.6
7	dt cm-1	251.42	305.71	306.28	354.28
8	Dq (ZZ) Cm-1	779.92	665.00	672.01	610.01
9	Dq (Xy) cm-1	1220	1200	1208	1230
10	DQ Cm-1	29495.33	28075.46	28286.17	28121.29
11	DT Cm-1	-3405.48	-4140.84	-4148.56	-4798.72
12	DQ E Cm-1	33523.39	32961.65	33181.47	33783.77
13	DQ A Cm-1	17235.60	13168.42	13351.35	10845.83
14	μeff from spectral data B.M.	2.83	2.82	2.82	2.82
15	DT/ DQ	0.11	0.15	0.14	0.17

Table (6.6) Electronic spectral data and Relevant ligand field parameters for Square Planar Ni (II) Complex.

S.No.	Compound	Absorption bands Cm-1	Tentative assignments	10 Dq	D1 -1 cm	D2 -1 cm	D3 -1 cm	LFSE K.cal/ Mole
1	[Ni(C11 H13 N3 O3 S)2 cl2	17600	1A1g---> 1 1A2g (v1)	19700	21300	6430	2137	67.54
		21230	1A1g---> 1 1B1g (v2)					
		24127	1A1g---> 1 Eg (v3)					

Table (6.7) Electronic spectral data and calculated transition energies of the spin allowed bands

in Octahedral Cobalt (II) Complexes.

S.No.	Compound	Method & Calculation	$4T_{2g}(F)$	$4A_{2g}(F)$	$4T_{1g}(P)$	10 Dq Cm-1	B35 Cm-1	β35 Cm-1	SV Cm-1	SV%	LFSE K CaL/Mole
1	CO (H2O)6 ++	Expt.	8100	16000	19400	-	-	-	-	-	-
		(b) Fitted	Fitted	17314	Fitted	9215	827.7	0.85	+1314	-	15.78
		(c) Fitted	7456	Fitted	Fitted	8543	868.7	0.90	-644	-	14.64
		(d) Fitted	6927	14827	Fitted	7900	740.0	0.76	-1173	-	13.54
2	[CO (C11 H13 N3 O3 S)3]Cl2	Expt.	9450	19120	21450	-	-	-	-	-	-
		(b) Fitted	Fitted	20143	Fitted	10698	883.2	0.91	=1023	5.07	18.32
		(c) Fitted	8943	Fitted	Fitted	10175	915.6	0.94	-507	5.67	17.43
		(d) Fitted	8470	18137	Fitted	9670	814.7	0.84	-983	5.41	16.57
3	[CO (C11 H13 N3 O3 S)3]2H2O	Expt.	9140	18400	20400	-	-	-	-	-	-
		(b) Fitted	Fitted	19460	Fitted	10330	830	0.855	+1060	5.76	13.77
		(c) Fitted	10893	Fitted	Fitted	8471	801	0.825	+1753	19.18	16.23
		(d) Fitted	Fitted	Fitted	Fitted	9260	758	0.781	-1924	9.43	15.87

Method Observed and calculated Transition Energies

Calcul-$4T_{1g}$ (F)------>

ation $4T_{2g}$ (F): $4A_{2g}$ (F): $4T_{1g}$ (P):

Table (6.8) Electronic spectral data and calculated transition energies of the spin allowed bands in Octahedral Cobalt (II) Complexes.

S.No.	Compound	Method &	Observed and calculated Transition Energies Calcul-4T1g (F)----> ation 4T2g (F):	4A2g (F):	4T1g (F):	10 Dq Cm-1	B35 Cm-1	β35 Cm-1	SV Cm-1	SV%	LFSE K CaL/ Mole
4	[Co(C11 H13 N3 O3 S](NO3)2	Expt.	9420	21420	19110	—	—	—	—	—	—
		(b)	Fitted	Fitted	22100	11685	797	0.82	+2990	15.64	20.02
		(c)	10470	Fitted	Fitted	10170	914	0.942	+1050	11.14	17.43
		(d)	Fitted	20110	Fitted	9670	818	0.843	-1309	6.11	16.61
5	[Co(C19 H19 N3 O4 S)cl2]	Expt.	9120	20430	18430	—	—	—	—	—	—
		(b)	Fitted	Fitted	16418	10312	833	0.858	-2011	10.91	17.67
		(c)	11770	Fitted	Fitted	9796	865	0.892	+2651	29.06	16.78
		(d)	Fitted	18629	Fitted	9310	766.66	0.790	-1800	8.8	15.96
6	[Co(C19 H19 N3 O4 S(NH3)2]	Expt.	9150	18430	20480	—	—	—	—	—	—
		(b)	Fitted	20735	Fitted	10300	834	0.86	+2305	12.51	17.70
		(c)	11522	Fitted	Fitted	9300	768	0.791	+2372	25.92	15.94
		(d)	Fitted	Fitted	18575	9280	764	0.787	-1905	9.30	15.90
7	[Co(C19 H19 N3 O4 S)(CH3COO)2]	Expt.	9100	18160	20360	—	—	—	—	—	—
		(b)	Fitted	19131	Fitted	10335	833	0.858	+971	5.34	17.70
		(c)	11700	Fitted	Fitted	18325	867	0.893	+2610	28.68	31.40
		(d)	Fitted	Fitted	18160	9060	748	0.771	-2200	10.80	15.53
8	[Co2(C19 H19 N3 O4 S)2cl4]H2O	Expt.	9000	18100	20000	—	—	—	—	—	—
		(b)	Fitted	19156	Fitted	10165	811	0.836	+1146	6.36	17.41
		(c)	9354	Fitted	Fitted	9580	848	0.874	+354	3.93	16.42
		(d)	Fitted	Fitted	19680	11000	734	0.756	-320	1.6	18.85

Table (6.9) Energy parameters for Cobalt (II) Complexes.

S.No.	Parameters	[CO(C11 H13 N3 O3 S)3]cl2	[CO(C11 H13 N3 O3 S)3](NO3)2	[CO(C11 H13 N3 O3 S)3]2H2O
1	V3/V1	2.26	2.23	2.27
2	V2/V1	2.02	2.013	2.02
3	V1/B	10.69	11.01	11.81
4	10 Dq from method (d)	9670	9260	9690
5	(Cg)	1.85	1.85	1.85
6	Dq/B	1.09	1.15	1.21

Table (6.10) Energy parameters for Cobalt (II) Complexes.

S.No.	Parameters	[CO(C19 H19 N3 O4 S)cl2]	[CO(C19 H19 N3 O4 S)(NH3)2]	[CO(C19 H19 N3 O4 S) (CH3 COO)2]	[Co2(C19 H19 N3 O4 S) 2CL4]H2O
1	V3/V1	2.24	2.238	2.237	2.22
2	V2/V1	2.02	1.95	1.99	2.001
3	V1/B	10.94	10.97	10.92	11.09
4	10 Dq from method (d)	9310	9280	9060	11000
5	(ß)	1.85	1.85	1.84	1.87
6	Dq/B	1.17	1.11	1.08	1.35

10 Dq, and λ in the relationship $\mu_{eff} = \mu_{s-o} \left(1 - \dfrac{4\lambda}{10\ Dq}\right)$

μ_{so} is Spin only value (2.84 B.M.) and spin obrit coupling constants value (λ) are calculated from spectral data. Higher value of magnetic moment in the complexes can be explained on the basis of octahedral symmetry involving high degree of orbital contribution due to three fold orbital degeneracy of 3 A2g ground state.

Electronic Spectral Studies:-

Electronic spectra of [Ni (C11H13N3O3S)2] Cl2 complex show sharp absorption bands around 17600, 21230 and 24127 cm -1 which are tentatively assigned to 1 A1g --> 1 A2g (γ_1); 1 A1g--> 1 B1g (γ_2) and 1 A1g --> 1 Eg (γ_3) transition respectively favouring square planar geometry(14). The maxima of γ_2 band of the complex represent the magnitude of crystal field splitting i.e. the energy separation between d (x2-y2) and dxy orbitals(15).

The five degenerate d-orbitals of the metal ions splits into four defferent levels of symmetries(16). b1g (dx2-y2); b2g (dxy), eg (dxz, dyz) and a1g (dz2) and related to three different parameters Δ_1, Δ_2 and Δ_3, depicted in figure. Values of different ligand field parameters Δ_1, Δ_2, Δ_3 have been calculated by the relationship using F2 = 10 F4 = 600 and 10 Dq = (γ_1 + 3.5 F2) where γ_1 is the first (d-d) spin allowed band and B and C are taken as 700 cm -1 and 3700 cm -1 respectively.

$$E \ (\ 1 \ A1g \ ---> \ 1 \ A2g \ ) \ (\ \gamma_1) = \Delta_1 - C$$

$$E \ (\ 1 \ A1g \ ---> \ 1 \ B1g \ ) \ (\ \gamma_2) = \Delta_1 + \Delta_2 \ - \ (\ 4B \ +C)$$

$$E \ (\ 1 \ A1g \ ---> \ 1 \ Eg \ ) \ (\ \gamma_3) = \Delta_1 + \Delta_2 \ + \Delta_3) - (\ 3B \ + \ C)$$

--   b1g (x2 - y2)

Δ_1

--   b2g (xy)

Δ_2

--   eg (xz.yz)

Δ_3

--   a.g (z2)
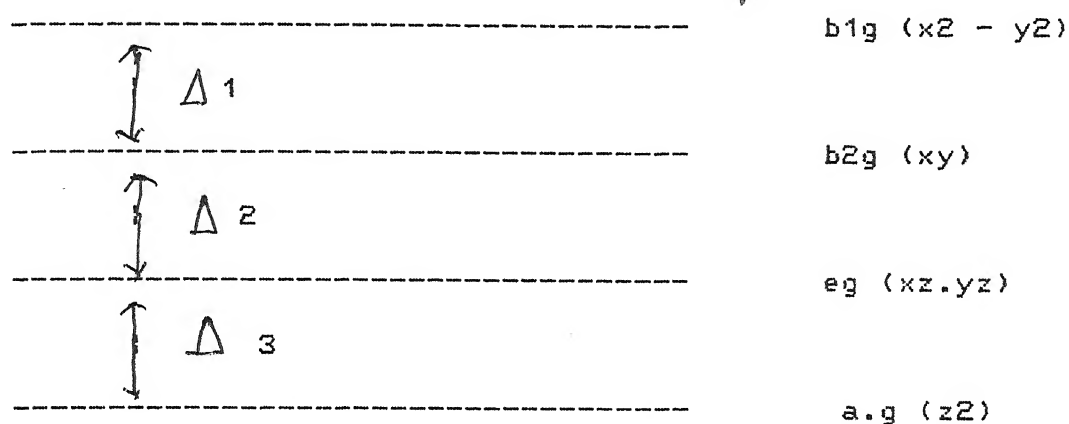
Fig = Metal (d) orbital energies for typical Nickel (II) square-planar complexes.

The calculated values are in asgreement with the reported value for square planar geometry(17-18).

Nickel (II) Tetragonally distorted Octahedral complexes:-

The electronic spectra of the solid complexes in Mgo, are very similar, showing similarities in their structures. Three bands are observed in the regions 8900-10600, 14000-17000 and 24000-27000 cm -1 which are assigned to the 3 A2g ---> 3 T2g (F); 3 A2g ---> 3 T1g (F) and 3 A2g ---> 3 T1g (P) vibrations,

respectively in the spectra of Ni (II) complexes. In addition to these bands a weak shoulder in the range 12000-12600 cm -1 has also been observed which may be considered the split components of 3 T2g. The band positions suggest the octahedral geometry of the six coordinate complexes(19-20).

On the basis of the band positions magnetic moments and the calculated values of ν_2 / ν_1, 10 Dq, B and β using different procedures (a) (b), (c) and (d) have been calculated. It was noticed tha only procedure (c) gives the best fit results, which further confirmed octahedral symmetry around Ni(II) complexes (23-24). The Racah parameter values have been found to decrease of the free ion value (1040 cm -1). This could be due to distortion of the octahedral symmetry in the complexes.

The higher values of ν_2 / ν_1 and ν_3 / ν_2 clearly suggest considerable tetragonal distortion from octahedral stereo-chemistry in a cubic field. It arises due to splitting of first absorption band(1) as 3 B1g-->3Eig($\sim$9400 cm -1) and 3 B1g --> 3 B2g ($\sim$12500 cm -1). The transition (ν_2) corresponds to DqL and separation of ν_1 and ν_2 is to the Ist order, 35/4 dt. Where Dt is related to the inplane and out of plane field strengths Via Dt = 4/7 [Dqxy- Dqz)] where Dq(xy) and Dq/z are inplane (xy) and out of plane (z) field strengths respectively (Dqxy = DqL) and Dq/B= 2.45; The redial parameter has been calculated from the splitting of —

$$4\ T_{1g}\ (F) \begin{cases} \longrightarrow 4\ A_{2ga}\ (V4);\ (\ -\ 4\ DS\ +\ 2\ Dt) \\ \longrightarrow 4\ E_{gb}\ (V3);\ (\ +\ 2DS\ +\ 3/4\ Dt) \end{cases} \quad separation$$

(6 DS – 5 Dt/4) with the combind use of crystal(25) field and normalised spherical harmonic Hamiltonian NSH parameters (26) equatorial field strength DQE and Axial field strength DQA have been calculated. The results suggest the higher field strength in Xy – plane (27).

Equatorial and axial field strength are ralated by the equations-

$$Dt = 4/7\ [\ Dq\ (xy)\ -\ Dq\ (z2)\ ] \qquad\qquad (i)$$

$$DQ = \sqrt{21}\ [\ 6\ Dq(xy)\ -\ 3.5\ Dt\ ] \qquad\qquad (ii)$$

$$DT = 3.5\ \sqrt{15}\ dt \qquad\qquad (iii)$$

Cobalt (II) complexes :- (Magnetic Studies) The magnetic moment of the Co (II) complexes (4.78 – 5.20 B.M.) are close to the value required for octahedral structure. Due to the incomplete quenching of the orbital contribution to the magnetic moment and mixing of orbital contribution to ground state $4\ T_{1}\ g$, both by spin Orbit coupling and by the magnetic field the value of Lande's splitting factor(g') decrease from 2.00 to 1.85-1.87 in the present complexes(28), (g) is related to Dq by

$$(g) = 2\ (1\ -\ \frac{4\lambda_0}{10\ Dq}\ )$$

where λ_0 is spin orbit coupling constant which is 172 cm -1 for free cobalt (II) ion.

Electronic Spectral Studies:- The reflectance spectra of Co(II) chelates consist of three bands in the region (8000-10000 cm -1); (16000-20000 cm -1) and (21000-23000 cm -1) which can be assigned to the transitions.

4 T1g (F) ---> 4 T2g (F); 4 T1g (F) ---> 4 A2g (F) and 4 T1g (F) ---> 4 T1g (P) respectively. The lowest and highest energy bands can therefore, be assigned as the ν_1 and ν_3 transitions while the middle one may be considered to arise either due to splitting of ν_3 band or may be due to the appearance of ν_2 transitions(29).

These bands suggest tetragonal distortion stereo chemistry for the Co (II) chelates(30). Using these transitions and the Konig equations for d7 ion different values of the ligand field parameters have been evaluated. The ratio ν_3/ν_1 and ν_2/ν_1 are found in the range (2.0-2.27); (1.90-2.01) respectively which lie with in the limit reported for tetragonally distorted octahedral cobalt (II) complexes(31-32). Different values of Dq, B, β also confirm the same geometry(33).

IR Studies:- The structurally important IR bands like $\nu_{(C=O)}$ $\nu_{(-N=N)}$; $\nu_{(>C=S)}$; $\nu_{(CH=N)}$; $\nu_{(M-O)}$ and $\nu_{(M-N)}$ have been assigned which throw light on structural features of the complexes.

The sharp bands at 3400 $\nu_{as NH2}$ and 3320 (ν_{S-NH2}) cm -1 in the IR spectrum of the ligand remains more or less unaltered in the complexes indicating non participation of the terminal --NH2 group in coordination.

Table (6.11) Tentative assignments of frequencies in cm-1 of Ni (II) Complexes.

S.No.	Complex Compound	NH stretch	ν(C=N)+ CH-Benzene in plane / NH-Bend-ing plane	ν(C=S)+ ν(CN)	>C=O	ν(C=S) Thio-Urea	(NH)out of plane	ν(M-O)	ν(M-N)/ν(M-S)
1	[Ni(C11 H13 N3 O3 S)2]Cl2	3350 vs 3260 s	1610 s 1390 m	1290 m 1250 s	1600 m	800 ms 1210 m	640 m	510 m	450m/400m
2	[Ni(C11 H13 N3 O3 S)2(NH3)2]Cl2	3360 s 3010 m	1600 s 1380 m	1280 ms 1230 s	1610 m	810 ms 1280 vs	650 m	500 m	460w/430w
3	[Ni(C11 H13 N3 O3 S)2(NO3)2]	3330 s 3290 m	1590 s 1410 m	1290 m 1270 s	1610 m	800 ms 1200 vs	650 m	510 w	460w/425w
4	[Ni(C11 H13 N3 O3 S)2(H2O)2]SO4	3340 s 3230 s	1610 s 1390 m	1300 m 1250 s	1600 m	800 ms 1210 m	640 m	510 w	470w/430w
5	[Ni2(C19 H19 N3 O4 S)2]Cl4	3360 vs 3260 m	1605 m 1380 m	1310 vs 1250 s	1630 m	740 ms 1190 s	650 m	500 w	520w/425w
6	[(C11 H13 N3 O3 S)]	3400 ms 3300 m 3200 m	1640 m 1410 m 1460 m	1350 s	1680 s	805 s 1220 m	680 m	-	Z
7	[(C19 H19 N3 O4 S)]	3360 m 3400 ms 3220 m	1640 m 1410 m 1460 m	1370 vs	1700 s	810 m 1220 m	670 m	-	-

Table (6.12) Tentative assignments of frequencies in cm-1 of Co (II) Complexes.

| S.No.	Complex Compound	NH stretch	ν(C=N)+ CH-Benzene in plane / NH-Bending in plane	ν(C=S)+ ν(CN)	>C=O	ν(C=S) Thio-Urea	(NH)out of plane	ν(M-O)	ν(M-N)/ν(M-S)
1	[Co(C11 H13 N3 O3 S)]Cl2	3340 m 3200 m	1600 m 1380 m	1315 s 1280 m	1640 s	800 ms 1200 vs	630 m	500w/480w /430w	
2	[Co(C11 H13 N3 O3 S)3]2H2O	3350 vs 3170 m	1580 m 1385 m	1310 s 1290 ms	1645 s	810 ms 1200 vs	635 s	490w/460w /430w	
3	[Co(C11 H13 N3 O3 S)3](NO3)2	3360 vs 3180 m	1595 m 1380 m	1330 m 1280 vs	1630 s	800 ms 1200 vs	630 m	500w/460w /430w	
4	[Co(C19 H19 N3 O4 S)Cl2]	3340 m 3200 m	1590 s 1385 m	1360 s 1300 m	1630 s	740 ms 1180 s	635 w	490w/460w /430w	
5	[Co(C19 H19 N3 O4 S)(NH3)2]	3340 m 3200 vs	1590 s 1390 m	1360 s 1280 m	1640 s	735 ms 1180 s	635 w	480w/450w 425w	
6	[Co(C19 H19 N3 O4 S)(CH3 COO)2]	3360 s 3200 vs	1610 m 1390 m	1350 m 1300 vs	1630 s	730 ms 1180 m	640 w	480w/440w /420w	
7	[Co2(C19 H19 N3 O4 S)2Cl4]H2O	3350 s 3190 m	1620 m 1390 m	1290 m 1230 s	1640 s	730 ms 1170 m	640 w	480w/450w /400w	
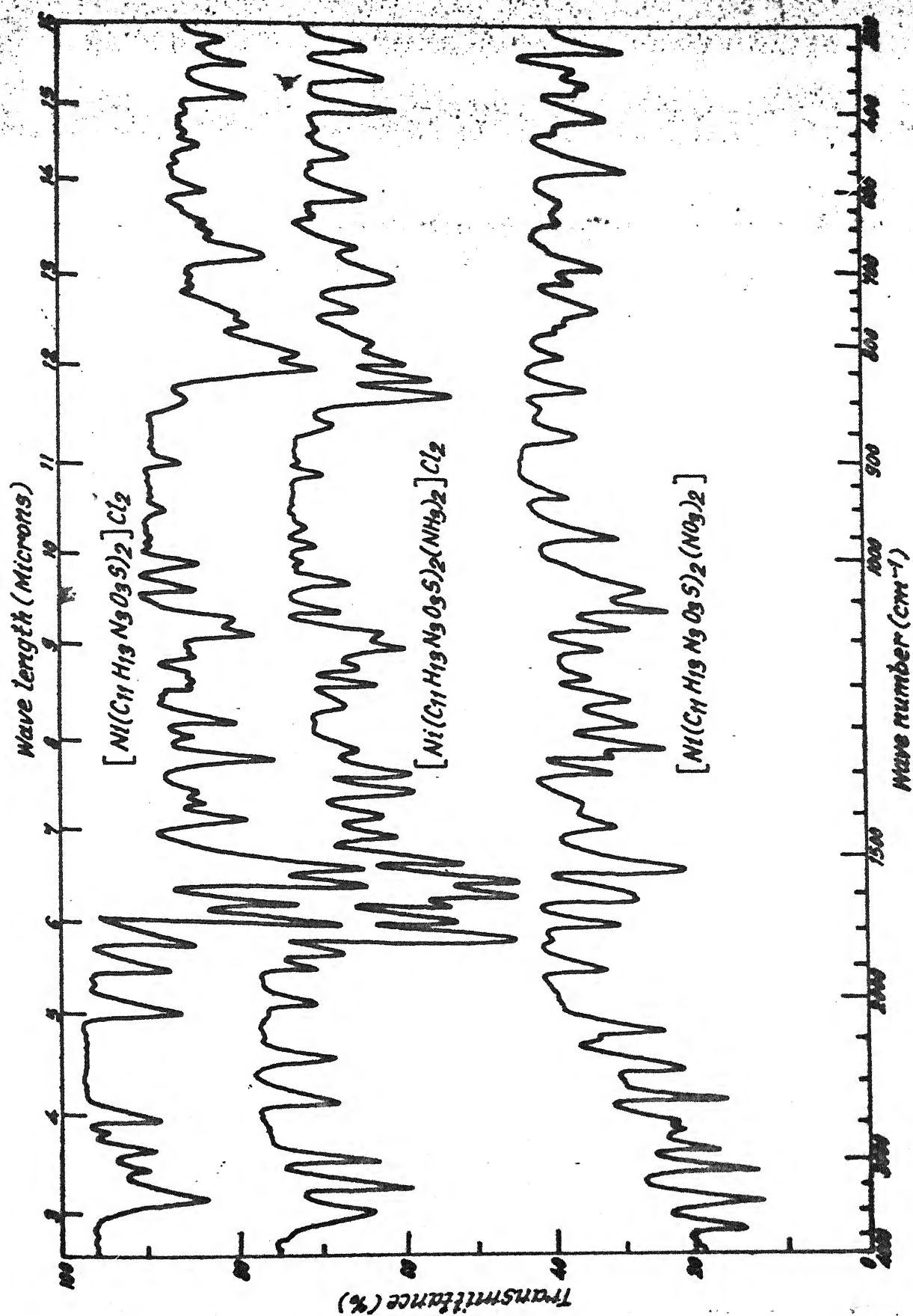
Fig. (6.1) : I.R. Spectra of Ni (II) complexes.
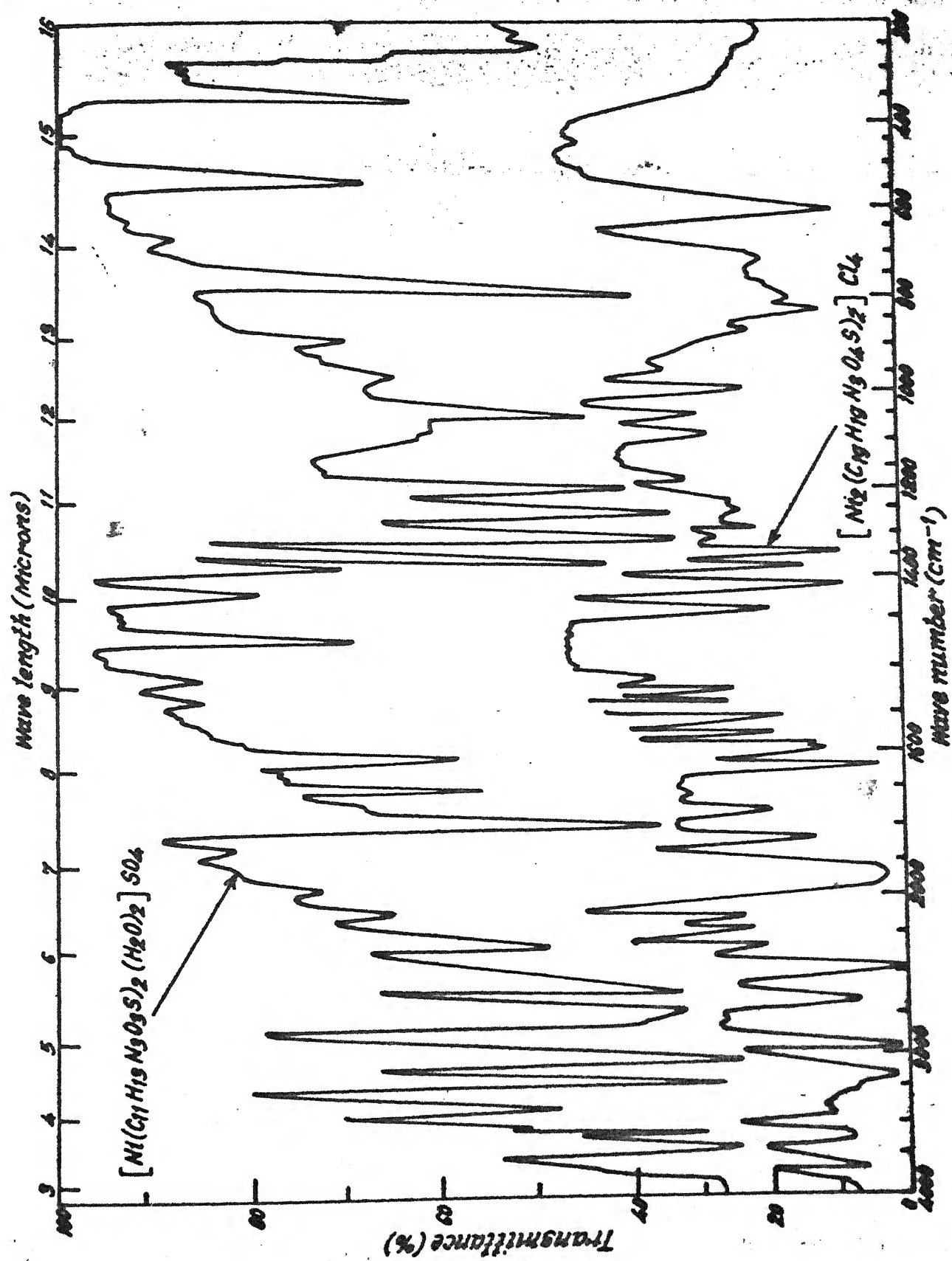
Fig. (6.2): I. R. Spectra of Ni(II) complexes.

Coordination through Thio Keto sulphur:-

Absorption bands at 1370, 1220, 805 and 710 cm -1 have been assigned to CS' stretching frequencies. Similar assignments are made earlier(34-36). These vibrations are lowered in the spectra of (C19H19N3O4S) complexes under study indicating involvement of s-atom in the complexation. In (C11H13N3O3S) complexes the frequency due to > C=S modes remain unaffected, showing its non involvement in chelation(37-38). The position of new band at 660 cm -1 in these complexes suggest the presence of (C-S-M) bonding(39-40).

Coordination through azomethine Nitrogen:-

The qualitative difference between the IR spectra of the free ligand and the complexes are discussed with a view to ascertaining the mode of attachment of the ligand to the metal. A band at 1635 cm -1 (C11H13N3O3S) and 1630 cm -1 (C19H19N3O4S) in the free ligand spectrum suffer a negative shift in the complexes suggesting coordination through azomethine nitrogen(41). The spectra of the ligand and complexes show sharp bands around 1110 cm -1 which may be assigned(42) to α(NH2) + β(NH2)

Coordination through carbonyl oxygen:-

Infra red spectrum of the free lignads show strong frequencies at 1690 cm -1 (C11H13N3O3S) and 1700 cm -1 (C19H19N3O4S) due to the Keto carbonyl, which on complexation show downward shiffs (20-50 cm -1) indicate coordination by the carbonyl group (43-45).
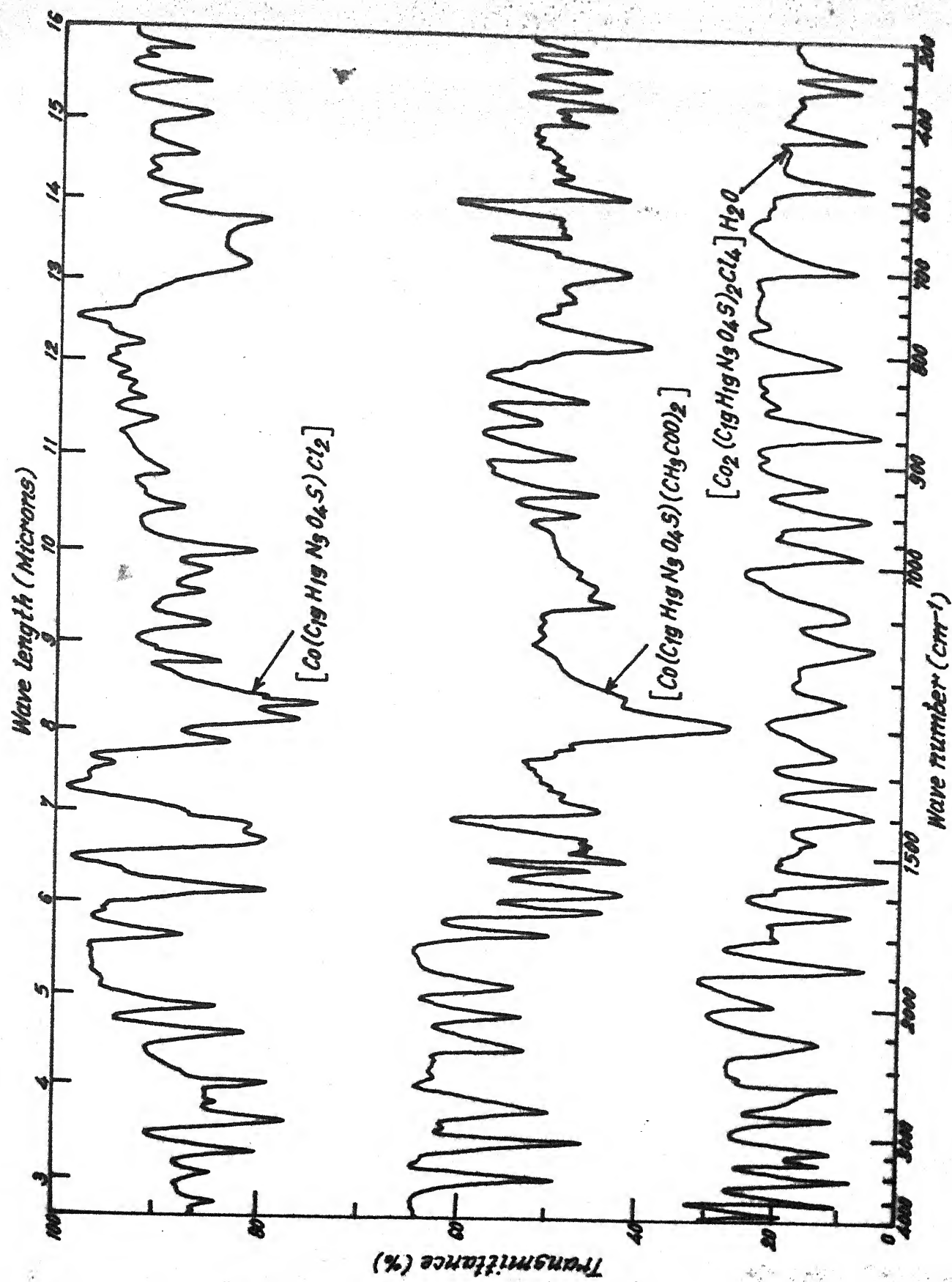
Fig. (6.3) : I.R. Spectra of Co(II) complexes.

Far infra red spectra:- The presence of coordinated water molecule is shown(46) by the occurence of broad band near 3400 cm -1 followed by two weak bands at $\sim$ 860 and $\sim$ 770 cm -1 assignable to OH stretching rocking, and wagging vibrations respectively(47).

In order to ascertain the nature of nitrate, whether it act as mono or bidentate in the complexes, a comparative study has been made. The complex [Ni (C11H13N3O3S)2 (NO3)2] show bands at 1380 and 1370 cm -1 revealing the presence of NO3 group.

The absorption at 1450 and 1240 cm -1 have been assigned to $\gamma_1(NO)$ and $V_4(NO2)$ asymmetric stretching respective vibrations(48-50), which inferred the presence of monodentate nitrate group in the complex.

Spectra of the complexes are very similar showing similarities in their structures. The bands appearing the far infrared region which have not been found in the spectra of free ligands have been assigned to $V_{(M-N)}$ $V_{(M-O)}$ $V_{(M-C1)}$ and $V_{(M-S)}$ vibrations(51). The appearance of metal chlorine stretching frequencies in the region 280-270 cm -1 also supports the octahedral stereo chemistry of Ni (II) and Co (II) complexes (52-59).

REFERENCES

CHAPTER-- VI

1. E.Sinn and C.M.Haris - Coord. chem. Rev. (1969) 4. 391.

2. H. Milburn. M..Truter and B.L.Vickery - J.chem. Soc. Dalton. Trans. (1974) 841.

3. H.E.Grey and C.J.Ballhausen -J. Am. Chem. Soc.(1963),85,260.

4. M.L.Gupta and K.K.Pande - J.Ind. Chem Soc. 34,62, (1965).

5. H.M.Irving and H.S.Rassotti - J.Am.chem. Soc. (1954),76, 2904.

6. M.Gerloch, J.Kohl, J.lewis and W. Urland-J. chem. Soc.(A) 3269 3283 (1970).

7. S.S.Sandhu, B.S.Manhas, M.R.Mittal and S.S.Parmar Ind. J-chem. 23 A (1984) 221.

8. R.C.Mehrotra etal- Ind.J-chem.11 (1973) 814.

9. P.R.Shukla , Gopal Narain and G.Mishra - Ind. J. chem. 23 A (1984) 253.

10.A.D.Damodaran, F.M.Ichaporia and G.S.Rao - J. Ind. chem. Soc. (1968), 45, 1673.

11.B.N.Figgis and J.Lewis - prog. inorg. chem. (1964), 6,37.

12.M.C.Day and J.Selvin - "Theoretical Inorganic chemistry - Reinhold New York 1962 p. 325.

13.R.S.Nyholm - chem. Rev. (1952), 53, 282.

14.Nitya nand Saha and N.G.Gayen - J. Ind. chem Soc.57 (1980), 548.

15.P.R.Shukla and Renu Takoo - Ind J. chem. 20 A (1981), 306.

16.P.L.Goggin, R.J.Good fellow and F.J.B.Reed -Jour. chem. Soc. Dalton Trans (1972), 1298.

17.A.R.Lathem V.Hanscall and H.B.Gray- Inorg. chem 4 (1965),788.

18.M.P.Teotia, J.N.Gurutu and V.B.Rana- Ind. Jour.chem 20A,

19. L.E.Orgel -J.chem. phys. (1955) , 23, 1004.

20. (a) Y.Tanabe and S.Sugano - J phys. Soc. Japan (1954), 9, 766.

    (b) M.A.Ali,U.Monir and M.H.Uddin -Ind. J.chem.(1985) 24, 358.

21. (a) M.N.Mokerjee, R.V.Singh and J.P.Tandon -Ind-J- chem.
    (1982) 21,388.

    (b) E.onig - Struct Bonding (1971), 9, 175.

22. A.B.P.Lever - "Inorganic electronic spectroscopy"- Elsevier,
    Amsterdam (1968), p.212.   ·

23. L.Saceoni - Transition metal chemistry- (1968), 4, 212.

24. A.B.P.Lever - J Chem. Educt, (1968), 45, 711.

25. R.Krishna murthi, W.B.Schaap and J.R.Perumareddi - Inorg.
    chem. 6 (1967), 1338.

26. A.B.P.Lever - Coord. chem. Rev. 3 (1968), 119.

27. D.E.Billing and A.E.underhill- J.inorg. Nucl. chem. (1968) 30,
    2147.

28. P.W.Selwood - Magnetochemistry - Interscience publisher , N.Y.
    (1953).

29. (a) R.L.Carlin -Trans. Metal. chem. vol. 1, Marcel Dekkar -
    N.Y. (1965) p.2.

    (b) G.L.Chaudhri etal -Jour.ind. chem. Soc. 67 (1990) 340.

30. B.Singh,Lakshmi and Umesh agarwal- Inorg. chem.(1969),8,2341.

31. K.C.Patel and I.E.Gold bers-jour. Inorg. nucl. chem. 34(1972),
    637.

32. F.A.Cotton, M.Goodgame and M.L.Zwelgame - Jour. Am.chem. Soc.
    83 (1961), 4690.

33. A.B.P.Lever and D.Ogden - J.chem Soc. (A) 1967, 2041.

34. L.J.Bellamy and P.E.Raogarsh - J.chem. Soc. (1960) 2218.

35. I.Suzuki-Bull. chem. Soc. Japan 35(1926) 1286, 1449, 1456.

36. G.R.Burns -Inorg. chem. 7(1968) 277.

37. Sanjay sen Gupta and N.K.Kaushik- Ind. Jour. of chem. 26A,175 (1987)

38. (a)R.Kellner, G.nikolov and N.Trendafilova - Inorg. chim. Acta 84 (1984) 223.

   (b)J.R.Dyer- Application of absorption spectrscopy of organic compound - Prentice Hall of India, New Delhi- (1969) p.89.

39. M.S.Patil and J.B.Shah - J. Ind. chem. Soc. 58 (1981) 944.

40. N.B.Colthup,L.H.Daly and S.E.wiberly- "Introduction to Infrared and Raman spectroscopy"(Academic press New York) (1964) 311.

41. M.J.M. Campbell - Coord chem. Rev. 15 (1975) 311.

42. M.J.M.Mostafa, A.M.shallaby and A.A.Elasmy - J.inorg. nucl.chem. 43 (1981) 2992.

43. L.El.Sayed & M.F.Iskander - J.inorg. nucl. Chem. 33 (1971)435.

44. M.F.Iskander, A.M.El.Aggar, L.S.Retaat and L.El sayed - Inorg. chim. Acta 14(1975) 167; 16(1976) 147; 22(1977) 141, J. inorg. Nucl. chem. 38 (1976) 2209.

45. C.Pelizzi & G.Pelizzi - J chem.Soc. Dalton Trans (1980) 1970.

46. J.R.Ferraro -"Low frequency vibration of inorganic and coordination compounds " Plenum press. New York. (1971).

47. K.Nakamoto - "Infra red spectra of inorganic and coordination compounds" - wiley N.Y. (1963).

48. J.E.Fleming and H.Lyton - chemy. Ind. (1963) 1416.

49. C.C.Addison and W.B.Simpson - J chem. Soc. (1965) 598.

50. A.B.P.Lever- Inorg. chem. 4 (1965) 1042.

51. M.M.Mostafa, A.M. Shallaby and A.A.Elasmy - J inorg. nucl. chem. 43 (1981) 2992.

52. J.R.Allen & D.M.Brown - Jour. inorg. nucl. chem. 27(1965) 350

53. T.L.Brown and Kubota - jour Am. chem. Soc. 83 (1961) 4175.

54. M.Mashima -Bull. chem. Soc. Japan 37 (1974) 229.

55. Rajiv jain, Partibha Pandey and Sushma Jain - Jour. Ind. chem. Soc. 67 (1990) 350.

56. K.C.Malhotra R. Sharma Seema pant and N.Sharma -Jour Of Ind. Council of chemists Vol.IV 3 (1988) p.109.

57. Assignments for vibrational spectra of seven hundred Benzene derivatives G.Varsanyi - Vol. I John Wiley, New York (1974).

58. C.N.R.Rao- Chemical applications of I.R.Spectroscopy, Academic Press New York. (1963)'

59. L.J.Bellamy- The infrared spectra pf complex molecule- chapman and Hall , London (1975).

CHAPTER - VII

SYNTHESIS AND STRUCTURAL STUDIES OF SOME TRI AND DIVALENT Cr(III) Mn(III), Co(III) and Vo(II) complexes of Schiff Bases.

Introduction:- Chelating properties of certain antimicrobial agents with metal ions enable a broad under standing about the mode of their action, especially when metal chelation affects their biological activity chelation with metals ions may result on either enchanging, stabilsing or abolishing the bioactivity of these agents (1-3). Schiff base complexes has attracted a great deal of attention, they find use as algaecides(4-5) and plant growth regulators.6.Dodwad et.at(7) have made solution studies of Schiff base complexes with Oxo-cations. Dubsky et.at(8) have reported coordinated polymers of polymeric Schiff base. Polymeric Schiff bases with long chain and high molecular weight were prepared by Aspey(9) and also by Marvel et.al(10) Magnetochemistry of (d3) Chromium (III) both for square Pyramidal and trigonal bipyramidal have been discucussed by Wood(11). The magnetic moments for five coordinate chromium (III) ions generally correspond to three unpaired electrons(12-13). The lowering of magnetic moment is due to weak antiferromagnetic interactions Manganese(III) generally forms high spin complexes and values of magnetic, moment correspond to four unpaired electrons (S=2) in the range (14-15) 4.90-5.10 B.M. The main cause of this lowering has been attributed to antiferromagnetic interactions in dimeric com plexes. A small lowering (0.1 B.M.) of the magnetic moment may arise due to lowering of symmetry and spin orbit coupling, in several cases values of μ-eff have been found to be anion dependent(16).

Electronic spectra generally used in distinguishing the various possible geometries for four and six coordinate complexes of various d^m electronic configurations, with the exception of d^0 and d10 systems. Five coordinate species have distinct electronic spectra, but it is generally difficult to differentiate between square pyramidal and trigonal bipyramidal geometries due to the non rigid nature of such species. A number of reviews have been devoted to coordination chemistry of Schiff base metal complexes (17-21). The ligand field strength of sulphur has been found to vary more than that of any other donor atom(22-23). This is probably due to the variation of bonding effects according to whether the sulphur has two or three lone pairs as in thioketones $>$ C=S or mercaptide ions R-S' which allows ample scope for (M-S) π bonding. As a part of our study in search of some new Schiff base complexes with possible biological activities we report here the preparation and characterisation of vanadyl(II) chromium(III), Manganese(III) and cobalt(III) complexes with α --N- methyl -S- Benzyl -β-N- 2:5 Dimethoxy (Phenyl glyoxal) methylenedithio -carbazate α -N-methyl-S-Benzyl-β-N-2-Hydroxy-5-Carboxy-phenyl glyoxal fmethylene dithio-carbazate, α -N-methyl S-Benzyl-β-N-2-amino Benzophenone methylene dithio carbazate,and 2:5-Dimethoxy phenyl glyoxal thiosemicarbazone.

Chromium complexes:-

1. [Cr (C19H20N2O3S2)2] Cl3 - It was prepared by mixing ethanolic solution of Crcl3. 6 H2O (1.32 gm. 0.005 M) with 0.01 M-α- N-methyl-S-Benzyl-β-N-2:5- Dimethoxy (phenyl glyoxal) methylene dithio carbazate. On refluxing for about an hour green

coloured mass was obtained it was filtered, washed successively water and alcohol and dried in vacuo.

2. $[Cr (C_{19}H_{20}N_2O_3S_2)_2] (NH_3)_3$ - A mixture of $CrCl_3$. 6 H_2O (0.05 M) and α -N- methyl-S- Benzyl - β -N-2:5-Dimethoxy (phenyl glyoxal) methylene-di-thio-carbazate (0.01 M) was refluxed for about two hour, after adjusting the pH~6.5 on water bath. The blue coloured precipitate so formed was filtered, washed with water-alcohol dried and collected over P_4O_{10} in vacuo.

3. $[Cr (C_{22}H_{21}N_3S_2)_3] Cl_3$ - To a ethanolic solution of $CrCl_3$. 6 H_2O (0.05 M) was added α -N- Methyl-S-Benzyl- β -N- (2 amino Benzophenone) methylene-dithio-carbazate (0.01 Mol.), and refluxed for 2-hour, after removing the solvent, the contents were concentrated on water bath, gave greenish coloured mass, which was filtered, washed and dried.

4. $[Cr (C_{22}H_{21}N_3S_2)_3] (NH_3)_3$ - To an ethanolic solution of chromium chloride hexa hydrate, a solution of α -N-Methyl-S-Benzyl- β - N - (2-amino Benzo phenone) methylene dithiocarbazate (0.01 M) was added followed by raising the pH by dilute solution of ammonia. The mixture was reflued for about 2-hour, when greenish coloured mass was separated out. It was then suction filtered through Buchnner funnel, washed with water and dried under vacuum.

5. $[Cr_2 (C_{18}H_{15}N_2O_4S_2)_2 Cl_4] Cl_2$ - The complex was prepared by refluxing ethanolic solution of chromium chloride hexa hydrate (0.05 M) and α -N- methyl-S- Benzyl - β -N-(2-Hydroxy-5-carboxy

phenyl glyoxal) methylene dithio carbazate in 1:1 molar ratio. The dark green mass obtained was filtered, washed with water and dried in vacuo.

Manganese (III) complexes:-

[Mn2 (C11H13N3O3S)4 (OH)2] 3H2 O - The complex salt was prepared by refluxing the manganese(III) dihydrate and 2:5- Dimethoxy phenyl glyoxal thiosemicarbazone in ethanol in 1:2 stoichiometric ratio for about 2-hour. After concentration and cooling for 2-3 days brownish coloured mass started appearing. It was filtered, washed and dried in vacuo.

Cobalt (III) complexes:-

1. [Co2 (C11H13N3O3S)4 Cl2] Cl4 - The complex was prepared by mixing ethanolic solution of 2:5- Dimethoxy phenyl glyoxal thiosemicarbazone and cobalt chloride hexahydrate in 1:1 stoichiometric ratio. After raising the pH to about 6.0 by dilute solution of ammonium hydroxide reddish brown coloured solution was obtained. It was refluxed for about an hour and then vigorous stream of purified air was passed into the reaction mixture for about 24 hours. A brownish red mass was obtained. The complex was filtered, washed sucessively with water and alcohol and dried in vacuo.

Vanadyl (II) complexes:-

1. [Vo (c11H13N3O3S)2] SO4 - The complex was prepared by refluxing ethanolic solution of vanadyl sulphate monohydrate (0.05 M) and 2:5-Dimethoxy phenyl glyoxal thiosemicarbazone (0.01 M) in 1:2 molar ratio for two hour and then keeping the resulting

solutions overnight. A bluish green coloured mass was obtained. It was filtered washed with water and dried in vacuum.

2. [Vo (C11H13N3O3S)2] Cl2 — The bluish green mass was obtained by refluxing vanadyl chloride and 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone in ethanol in 1:2 molar ratio. The filtered mass was washed, and dried over conc. H2So4 in vacumm desiccator.

Results and discussion:-

Chromium (III) complexes:- Magnetic susceptibilities of the chromium complexes were measured by a modified form(24) of Gouys balance, and found them paramagnetic. The magnetic moment lies in the range 3.66 B.M. -3.98 B.M. showing tetragonal distortion stereochemistry(25). The deviation I δV2,3 I between the calculated and experimental values also support the above contention.

Electronic spectral studies:- The values of molar conductance shows some of the complexes are electrolytic in nature.

The electronic spectra of CrIII) complex show three transitions 4 A2g(F) ---> 4 T2g(F) v1; 4 A2g ---> 4 T1g(F) (v_2) and 4 A2g(F) ---> 4 T1g(P) (v_3) in order of their increasing energy at around 17000-18000, 23000-25000 and 36000-38000 cm -1. If the field is further lowered to D4h symmetry these states further splits into (4 Eg + 4 B2g), (4 A2g + 4 Eg) and (4 A2g(P) + 4 Eg (P)) states respectively and therefore, six bands are expected in D4h symmetry(26). The splitting of band (I) and (II) indicate lowering of symmetry. The energy transitions are proposed by Barnum(27-28) and First spin allowed transition

Table (7.1) Analytical and magnetic data of Cr (III) complexes.

| S.NO. | Compound | Chemical analysis calcd /(Found) | | | | | | Magnetic data | | Stereo-chemistry |
		% C	H	N	S	Cl	Metal	Xm x10-6 CGSU Cgs Unit	μ eff B.M.	
1	[Cr (C19 H20 N2 O3 S2)2]Cl3	48.78 (48.13)	4.28 (3.97)	5.99 (5.38)	13.69 (12.93)	11.39 (10.80)	5.56 (5.15)	5514.82	3.66	H.S.0
2	[Cr (C19 H20 N2 O3 S2)2](NH3)3	51.52 (50.17)	5.19 (4.99)	11.07 (10.91)	14.46 (13.89)	– –	5.87 (6.87)	5800.4	3.72	H.S.0
3	[Cr (C22 H21 N3 S2)3]Cl3	59.48 (58.44)	4.73 (3.45)	9.46 (8.70)	14.41 (13.33)	7.99 (7.35)	3.9 (3.30)	5957.4	3.79	T.D.0
4	[Cr (C22 H21 N3 S2)3](NH3)3	62.06 (61.63)	5.64 (5.21)	13.16 (12.12)	15.04 (13.76)	– –	4.07 (3.70)	5769.3	3.71	T.D.0
5	[Cr2(C18 H15 N2 O4 S2)2 Cl4]Cl2	42.35 (41.12)	2.94 (2.20)	5.49 (5.02)	12.34 (11.82)	20.88 (19.73)	10.19 (9.76)	6639.64	3.98	T.D.0

H.S.0 – High Spin octahedral ; T.D.0 – Tetragonally distorted octahedral

Table (7.2) Analytical and magnetic data of Mn (III), Co(III) and vandyl complexes.

S.NO.	Compound	Chemical analysis calcd /(Found)						Magnetic data		Stereo-chemistry
		% C	H	N	S	Cl	Metal	$X_m \times 10^{-6}$ CGSU Cgs Unit	μ_{eff} B.M.	
1	[Mn2(C11 H13 N3 O3 S)4(OH)2]3H2O	41.71 (40.88)	4.73 (4.00)	13.27 (12.12)	10.11 (9.30)	— —	8.08 (8.35)	9982.63	4.88	T.D.B.O
2	[Co2(C11 H13 N3 O3 S)4Cl2]Cl4	37.74 (36.10)	3.71 (2.98)	12.00 (11.35)	9.15 (9.00)	15.22 (14.26)	8.42 (8.10)	202.12	0.22	T.D.B.O
3	[Vo(C11 H13 N3 O3 S)2]So4	37.87 (36.99)	3.73 (3.01)	12.05 (11.77)	13.77 (12.12)	— —	7.30 (6.90)	1294.12	1.72	TDM Sq Pya.
4	[Vo(C11 H13 N3 O3 S)2]Cl2	39.28 (38.00)	3.86 (3.15)	12.50 (11.92)	9.52 (8.42)	10.36 (9.75)	7.38 (6.10)	1419.15	1.84	TDM Sq Pya.

H.S.O – High Spin octahedral ; T.D.O – Tetragonally distorted octahedral

TDBO – Tetragonally distorted bridged octahedral;

TDM-Sq.Pyra. – Tetragonally distorted monomeric square pyramidal.

Table (7.3) Electronic Spectral data (Cm⁻¹_, Tentative assignments and ligand field parameters.

S.No.	Compound	Method of Calculation	4A2g ---> 2Eg(S.F) 4A2g->4B2g	4A2g(g) ---> 4T2g(F) V1	4A2g(g) ---> 4T1g(F) V2	4A2g ---> 4T1g(P) V3	B	β 35	δV Cm-1	δV %	LFSE K.Cal MOLE-1
1	[Cr (H2O)6]+3	Expt.	(S.F)	17400	24600	38000	-	-	-	-	-
		(a)	-	10 Dq	Fitted	38510	728.0	0.79	+510	1.39	-
		(b)	-	10 Dq	24000	Fitted	657.0	0.71	-600	2.50	-
		(c)	-	10 Dq	24530	38070	693.0	0.75	+70	0.23	-
2	[Cr (C19 H20 N2 O3 S2)2]Cl3	Expt.	13000	17200	23400	37180	-	-	-	-	-
		(c)	19740	10 Dq	23370	37210	598	0.65	+30	0.128	58.97
3	[Cr (C19 H20 N2 O3 S2)2](NH3)3	Expt.	12810	17000	23130	36748	-	-	-	-	58.28
		(c)	19080	10 Dq	23100	36768	591.86	0.644	+20	0.8	-

Table (7.4) Electronic Spectral data (Cm-1), Tentative assignments and ligand field parameters.

S.No.	Compound	Method of Calculation (S.F)	4A2g ----> 2Eg(S.F) 4A2g->4B2g (S.F)	4A2g(g) ----> 4T2g(F) V1	4A2g(g) ----> 4T1g(F) V2	4A2g(g) ----> 4T1g(P) V3	B	β_{35}	SV Cm-1	SV %	LFSE K.Cal MOLE-1
1	[Cr(C22 H21 N3 S2)3]Cl3	Expt.	13108	17570	24090	37183	–	–	–	–	–
		(c)	19300	10 Dq	23545	37728	570	0.620	+545	2.31	60.24
2	[Cr (C22 H21 N3 S2)3]NH3)3	Expt.	13215	17360	24500	38106	–	–	–	–	–
		(c)	19500	10 Dq	24350	38256	701	0.764	+150	0.061	46.29
3	[Cr2(C18 H15 N2 O4 S2)2Cl4]Cl2	Expt.	13347	17158	24218	37929	–	–	–	–	–
		(c)	19460	10 Dq	24200	37947	711.53	0.775	+18	0'07	45.73

Table (7.5) Ligand field and NSH Parameters for chromium (III) complexes   P. No. 149

S.No.	Parameters	[Cr(C11 H2O N2O3S2)2]C13	[Cr(C11 H2O N2O3S2)2](NH3)3	[Cr(C22 H21 N3S2)3]C13	[Cr(C22 H21 N3S2)3](NH3)3	[Cr2(C18H15 N2O4S2)2C14] C12
1	Dq B	2.87	2.87	3.08	2.47	2.41
2	F2 cm^{-1}	2041.80	2065.71	2081.09	2154.71	2132.80
3	F4 cm^{-1}	306.27	309.85	307.55	311.91	319.92
4	Dt cm^{-1}	480	478.85	509.94	493.71	435.54
5	DS cm^{-1}	-810	-808.07	-860.53	-799.39	-734.97
6	do cm^{-1}	2415	2409.23	2565.64	2433.36	2191.30
7	dπ cm^{-1}	315	314.26	334.65	273.33	285.81
8	D 1 cm^{-1}	4830	4818.46	5131.29	4866.72	4382.61
9	D 2 cm^{-1}	17200	17000	17570	17360	17158
10	D 3 cm^{-1}	840	843.55	892.42	729.01	762.18
11	Dq(xy) cm^{-1}	1720	1700	1757	1736	1715
12	Dq(z) cm^{-1}	880	862.01	864.60	872.00	952.80
13	Dq	38571.2	39040.03	40108.02	39791.10	40146.49
14	DT	6501.6	6486.02	6907.13	6687.30	5899.38
15	DS	5670	5656.49	6023.71	5595.24	5144.79
16	B 55	1.41	1.43	2.98	2.93	2.39
17	(1-ε) β35/55	0.46	0.45	0.20	0.26	0.33

Table (7.6) Electronic spectral data (cm-1) Tentative assignments, Ligand field and NSH Parameters for Cobalt (III) complexes.

S.No.	Compound	Transition	Assignments	B	10 Dq	C	Dq(XY)	Dt cm^{-1}
1	[Co2(C11 H13 N3 O3 S)4 Cl2]Cl4	1A1--->1A2ga 1T1g	8500	547.66	21906.4	2190.6	1416.6	442.28
		--->1Eg	16430					
			20300					
		1A1--->1B2g 1T2g	27475					
		--->1Eg(b)	31870					
		β -0.497;Dq(ZZ)	642.66	DT - 5990.68	DS - 4482.4			
		Dq E-46022.57; DQA	67281.98	DT/DQ - 0.112				
		DS-640.35						
		Dq-53109.04						

Table (7.7) Electronic spectral data (cm-1) , Tentative assignments ligand field and NSH—
parameters for Mn (III) complexes—

S.No.	Compound	Assignments and Energy parameters	Absorpti- on bands Cm—1	B 35 Cm—1	β 35 Cm—1	C Cm—1	10 Dq
1	[Mn2(C11 H13 N3 O3 S)4(OH)2]3H2O Spin forbidden		9648	770.70	0.682	3110.8	13790
		5B1g--->5A1g(ν1)	13790				
		--->5B2g(ν2)	21387				
		--->5Eg(ν3)	30665				

F 2 —1822 ;F4 —273.3 ; Dt — 473.37 ; DS — (—) 1451.04   do — 1288.99

dʎ— 3359.98; Dq (XY) — 1379; Dq — 30306.8; DT — 6411.79; DS — 10157.28

DQ E — 22722.192; DQA — 45476.01; DT/DQ — 0.211

Table (7.8) Electronic spectral Bands (Cm-1) Tentative assignments, Ligand Field and NSH
parameters for vanadyl)II) complexes.

S.NO.	Compound	Assignments and Energy parameters	Bands Energy	Dq	DS	Dt
1	[Vo(C11 H13 N3 O3 S)2]So4	2 B2----->2E (√1)	12670	1694.8	-2444.57	1067.25
		2 B2----->2B1(√2)	16948			
		2 B2----->2A1(√3)	21390			
		Charge Transfer	24480			
		DS-17118.99 DT - 14455.90; DQ-29465.08; DQ A- 63665.30				
		DQE - 12364.96 DT/DQ -0.4906				
2	[Vo(C11 H13 N3 O3 S)2]Cl2	2 B2----->2E (√1)	12705	1674	-2555.0	1058
		2 B2----->2B1(√2)	16740			
		2 B2----->2A1(√3)	21920			
		Charge Transfer	24460			
		DS -17885; DT-14330.61; DQ- 29041.78; DQ-62945.13				
		DQE- 12090.102; DT/DQ- 0.4934				

directly give 10 Dq the values of ν_2 and ν_3 were calculated using the standard equations which include configuration inteaction. The Racah parameter (B) may be calculated by four different methods as discussed by Koning(29).

$$1 = 10 \text{ Dq} \ldots \ldots \text{(I)} \quad \text{(a)} \quad B1 = \frac{(2 \text{ V1}^2 + \text{V2}^2 - 3 \text{ V1 V2})}{(15 \text{ V2} - 27 \text{ V1})} \quad \text{(II)}$$

(Fitting the second band)

$$\text{(b)} \quad B2 = \frac{(2 \text{ V1}^2 + \text{V3}^2 - 3 \text{ V1 V3})}{(15 \text{ V3} - 27 \text{ V1})} \quad \text{(III)}$$

(Fitting the third band)

$$\text{(c)} \quad B3 = \frac{(\text{V2} + \text{V3} - 3 \text{ V1})}{15} \quad \text{(IV)}$$

(Fitting the sum of second and third band)

$$\text{(d)} \quad B4 = 1/75, \text{ [(3V1} + \{ 25 (\text{V3-V2})2 - 16 \text{ V1}^2 \}] \text{ 1/2} \quad \text{(V)}$$

(Fitting the difference of third and second band)

But in the present complexes the value of B35 and B55 have been calculated by the expression.

$$B35 = \frac{(\text{V2} + \text{V3} - 3 \text{ V1})}{15}$$

(Fitting the sum of V2 and V3)

$$B55 = E (4 \text{ A2g} \longrightarrow 2 \text{ Eg}) = 9 B55 + 3 C - \frac{50 \text{ B } 55^2}{10 \text{ Dq}}$$

assuming (C = 4 B)

The value of B and β - depends significantly on the method adopted however the best fit method is (c) where the deviation is

of less order in V2, V3 observed and calculated. Nephelauxetic ratio (β 35) is determined by repulsion in both values of β 35 and β 55 indicate too much weak π- delocalisation of metal electrons and σ-type interaction between metal and ligand(30).

The octahedral stereochemistry of the complex has also been further confirmed from the low value of molar extinction coefficient, various values of ligand field parameters eg. Ds, Dt, DQ, DQA, DQE, dσ, dπ, D1, D2, D3 further support distorted octahedral structures(31-33).

Cobalt (III) complex [CO2 (C11H13N3O3S)4 C12] C14 :-

Magnetic Studies:- Complex is found to be diamagnetic. This behaviour of the complex ruled out the mixing of bivalent cobalt. The cobalt (III) complexes are usually diamagnetic irrespective of the geometry of the ligand field environment.

Electronic spectral studies:-

The electronic spectra of the complex show various bands in the region ~ 8500, 16430, 20300, 27475, and 31780 cm -1 out of the five bands two bands appearing at 16430 and 20300 cm -1 are characteristic of octahedral six coordinate trivalent cobalt(34). These bands have been assigned to the transitions 1 A1g-->1 A2g; --> 1 Ega --> 1 B2g and --> 1 Egb respectively. The first two bands are the split components of 1 T1g in which higher energy band is a shoulder and of low intensity. Like wise 1 T2g splits into two bands, the higher energy band assigned to 1 Egb, which is also found to be of low intensity. These observation indicate

deviation from octahedral stereochemistry with approximate D4 h symmetry. The values of Dq/B in the complex is close to Dq/B= 4.0 showing tetragonally distorted octahedral geometry.

By knowing the splitting of (I) excited term 1 T1g, and 1 T2g (II) which is 35/4 dt. and − 6 DS + 5/4 dt. respectively in octahedral symmetry, the value of different ligand field parameters Dt, DS, Dq (xy), Dq (z2) have been calculated (35).

Normalised Spherical Harmonic (NSH) Hamiltonian and its Applications:-

The square pyramid which confirms to C4 V point group symmetry can be compared to D4 h point group. This follows from the crystal field argument that the energy levels in a tetragonal complex are determined by the total potential along the Z − axis, regardless of whether this potential is equally or unequally distributed above and below the molecular plane(36). In case of a square pyramid, the potential below or above the Z-axis may be taken, as zero. On the basis of these arguments. Lever et. al (37) applied the newly developed theory of Normalised spherical Harmonic (NSH) Hamiltonian to find out the absolute ligand field parameters designated as Dq, DS, DT, DQA, and DGE in conjuction with the Racah interelectronic parameters, B and C. These parameters along with the ratio DT/Dq, Which measures the degree of distortion, project the true stereo − chemistry and nature of bonding in cubic and non cubic complexes.

These parameters have been fully capitalised to distinguish them from the conventional ligand field parameters Dq, DqE, DQA, DS and Dt, and the ralationship has been established between them (38).

The advantage of NSH Hamiltonian parameters are –

(i)   It take into consideration off-diagonal contribution to (dt).

(ii)   Parameters are independent of coordinate system.

(iii)   Can be compared with crystal field or angular overlap model (39-40).

NSH and classical parameters are related by

$$DS = -7\ DS$$
$$DT = (7\ \sqrt{15/2}\ )\ Dt$$
$$DQ = (6\ \sqrt{21}\ )\ Dq - (7\ \sqrt{21/2}\ )\ Dt.$$

It is to be noted that with this Hamiltonian the tetragonal distortion splits the eg and t2g levels of the octahedron in a fashion which obeys the centre of gravity rule for both DS and DT in contradiction to the classical approach. In the limit octahedral symmetry when DS and DT are zero, the tensor Hamiltonian Yields value of DQ which are greater than those of the classically used Hamiltonian by the factor (6   21). Two additional parameters derived from the spectra of tetragonal molecules such as ME 4 A2 are DqE and Dq (A), the magnitude of the crystal field parameter in the hypothetical octahedral ME 6 and MA 6, respectively (41-42).

NSH parameters are related to classical one.

$$DQ = (1/6)(4\ DQE + 2\ DQA)$$

$$DT = (1/3)\left(\frac{\sqrt{5}}{\sqrt{7}}\right)(DQE - DQA)$$

$$= (1/2)\left(\frac{\sqrt{5}}{\sqrt{7}}\right)(DQ - DQA)$$

$$= \left(\frac{\sqrt{5}}{\sqrt{7}}\right)(DQE - DQ)$$

These quantities make it clear that DQ is a measure of the average ligand field experienced by the metal ion, unlike the classical Dq which is a measure of the inplane ligand field.

DT/DQ measure degree of distortion. DT/DQ values generally lie in the range of 0.1 to 0.2 while the value of this ratio for a square planar complex is 0.4226.

The DQA has the significance of the field experienced by the metal ion along Z-axis. It is actually an average of the axial ligand field due to the absence of a ligand in the sixth position. In such a case where the field strength in the sixth position is Zero, the DQA has a magnitude of half the field strength of axial ligand.

The NSH absolute parameter can also be related to the MCclure Molecular parameters as

$$d\sigma = (1/28)(6\ DS - \sqrt{15}\ DT)$$

$$d\pi = (1/14)\left(3\ DS + 2\ \frac{\sqrt{5}}{\sqrt{3}}\ DT\right)$$

Where $d\sigma$ represents the difference between the antionding power
of the Z (σZ) ligand and σ antibonding power of the (X-Y) plane
ligand σL, $d\pi$ is thus similarly defines.

$$d\sigma = \sigma Z - \sigma L$$

$$d\pi = \pi Z - \pi L$$

The negative value of $d\sigma$ indicate that the σ - antibonding
capability of equatorial ligand is more than that of the axial
ligand and since $d\pi$ is positive, the π -bonding ability of
axial ligand is more than equatorial ligands.

DT/DQ value (0.112) indicate distortion in octahedral
geometry(43-44).

Manganese (III) complex:-

[Mn2 (C11H13N3O3S)4 (OH)2] 3 H2O - The magnetic moment
of the complex is (4.88 B.M.) which corresponds to d4 ion without
orbital contributions(45). Moreover the pairing of spin in
manganese complexes only occurs for compounds of strongest field
(CN-). However small lowering of magnetic moment from spin only
value of 4.94 B.M. may arise from the effects lowering in
symmetry(46) or spin orbit coupling.

Electronic spectral studies:-
The electronic spectra of the
complex shows number of bands at 9648, 13790, 21387 and 30665 cm-1
which have been assigned to spin forbidden, 5 B1g --> 5 A1g (ν_1);
5 B1g --> 5 B2g (ν_2) and 5 B1g --> 5 Eg (ν_3) transition in
order of increasing energy following Jahn-Teller(47) inter
electronic forces. The band observed at 21387 cm-1 is the
characteristic of octahedral stereo chemistry(48). Alternatively,

the spectral bands can be assigned in single electron transitions as $dz2 \longrightarrow d (X2-Y2)$; $dxy \longrightarrow d(x2-y2)$ and $dxy.dyz \longrightarrow d(x2-y2)$ respectively(49-52).

Therefore, the energy level sequence for C4V square pyramidal molecule can be drawn as 5 B1< 5 A1 < 5 B2 < 5 E. on the above basis the values of 10 Dq, B. β , F2 and F4 have been calculated using perumareddi equation(53). The value of DS, Dt, have been used up in calculating DS and DT. DQE and DQA correspond to degree of distortion by proposing equitorial and axial field strength.

Magnetic studies:- Vanadyl (II) complexes [Vo (C11H13N3O3S)2] SO4 and [Vo (C11H13N3O3S)2] Cl2 - Magnetic moment values of the complexes correspond to one paired electron and very close to spin only value for monomeric vanadyl (II) complexes(54-55).

Electronic spectral studies:- The vanadyl(II) complexes show three (d-d) transition of low intensity around 12000-13000 cm-1 16000-17000 cm-1, 21000-22000 cm-1 and 24000-25000 cm-1 (charge transfer), which have been assigned to Transitions (2 B2 --> 2 E) (dxy --> dxz.dyz); 2 B2 --> 2 B1 (dxy --> dx2-y2 and 2 B2 --> 2A1 (dxy --> dz2) using vanquichen-Borne and Mcglynn- scheme(56) as well as Ballhausen and Gray(57) for tetragonally distorted monomeric square pyramidal Vanadyl(II) complex. Similar scheme was also favoured by Selbin et.al(58); in lower symmetry vanadyl(II) complexes. The complexes show a broad visible band centered at 13510 cm-1 with shoulders on either sides. This suggest the low symmetry of the complex(59). The three bands observed in the electronic spectra may be assigned in an octahedral symmetry with tetragonal distortion(60-61).

Table(7.9) Assignments of IR frequencies in Chromium (III) Complexes.

S.NO.	Complex compounds	-OH / NH2	γ(C=N) and CH-Benzene Bending in plane	γ(C=S)+ γ(CN)	>C=O	γ(C=S) Thio Urea	NH out of urea	γ(M-O) / γ(M-N) / γ(M-S)
1	[Cr(C19 H20 N2 O3 S2)2]C3	-	1610 m / 1400 (m)	1620 ms	1620 vs	750 w	680 m	500w/470m /430m
2	[Cr(C19 H20 N2 O3 S2)2](NH3)3	-	1600 m / 1400 (m)	1625 ms	1640 vs	780w	680 m	510w/470m /440 m
3	[Cr(C22 H21 N3 S2)3]C13	-	1580 w / 1410 (m)	1625 ms	1640 vs	765 w	660 m	505m/475m /435 m
4	[Cr(C22 H21 N3 S2)3(NH3)3]	3180 s	1605 w / 1405 (m)	1630 ms	1630 vs	775 w	675 m	500w/470m /440 m
5	[Cr2(C16 H15 N2 O4 S2)2C14]C12	1340 w	1615 m / 1410 (m)	1620 ms	1550 s	780 w	675 m	510m/480m /440 m
6	(C19 H20 N2 O3 S2)	-	1630 m / 1440 m 1460 m	1300 s 1350 vs	1680 s	805 s 1220 m	675 m	-
7	(C22 H21 N3 S2)	-	1630 m / 1400 m 1440 m	1360 s 1310 s	-	810 s 1220 m	675 m	-
8	(C18 H15 N2 O4 S2)	2840 m 3500 m	1630 m / 1440 m 1400 m	1350 vs 1300 s	1680 s	805 s 1220 m	675 m	-

Table(7.10) Assignments of Mn (III), Co (III) and Vo (II) Complexes.

S.NO.	Complex compounds	ν(NH) Stretch	ν(C=N)and NH Bending in plane	CH-Benzene	ν(C=S)+ ν(CN)	C=O	ν(C=S) Thio Urea	NH out of urea	ν(M-N)/ ν(M-O)/ ν(M-S)
1	[Mn(C11 H13 N3 O3 S)4(OH)2]3H2O	3380 vs 3280 s	1605 (w)	3070 w 1590 s	1270 w	1640 m	810 s	680 m	500w/480m
2.	[Co2(C11 H13 N3 O3 S)4Cl2]Cl4	3300 s 3190 m	1600 m	3080 w 1580 s	1275 w	1660 w	815 s	670 m	505w/475m
3	[VO(C11 H13 N3 O3 S)2]So4	3300 s 3195 m	1605 w	3130 w 1560 m	1305 w	1650 s	815 s	670 m	490m/405w
4	[VO(C11 H13 N3 O3 S)2]Cl2	3310 m 3180 s	1605 w	3100 w 1615 s	1300 vs	1640 s	815 s	680 m	470m/405w
5	(C11 H13 N3 O3 S)	3400 ms 3290 m 3200 (m)	1635 m	1400 m 1450 m	1350 vs	1690 s	805 s 1220 m	680 m	—

Any band beyond 22000 cm-1 may be attributed to charge transfer or intra ligand transition.

The values of various ligand field and NSH-parameters DG, DT, DS, DGE, DGA, and DT/DG suggest tetragonal distortion in the complexes.

IR Studies:-

Chromium (III) complexes:- A broad band at 3440 cm-1 in the (C18H16N204S2) ligand is ascribed to ν(OH) vibration, lowered due to intra molecular OH-....O and O-H--- N hydrogen bonding. Disappearance of band in complexation indicative of deprotonation and formation of (C-O-M) bond. The band found in the spectra of ligand at about 1320 cm-1 shifts to higher frequency region 1340 cm-1 further support Bonding of (C-O-M) through phenolic oxygen atom.

The (CH=N) stretching frequency of the ligand observed at 1640 cm-1 shifts to 1620-1590 cm-1 in the complexes. The negative shift in frequency on complexation indicate(62-63) the bonding with the chromium ion.

New Bands at 470, 430 cm-1 observed in the spectra of metal complexes(64-65) are due to ν(M-N) and ν(M-S). Conclusive evidence of metal-oxygen bond is provided by a band~ 500 cm-1 in the complexes. A sharp band observed ot 2900 cm-1 due to (N-H) remain unaltered in the spectra of complexes.

The IR spectra of the ligands show very strong absorptions at 1680 cm-1 (C=O). The aldehydic (C=O) and the phenolic (C-O) both split into two, .the aldehydic (C=O) show up at 1680 and 1640 cm-1 where as phenolic (C-O) can be spotted out
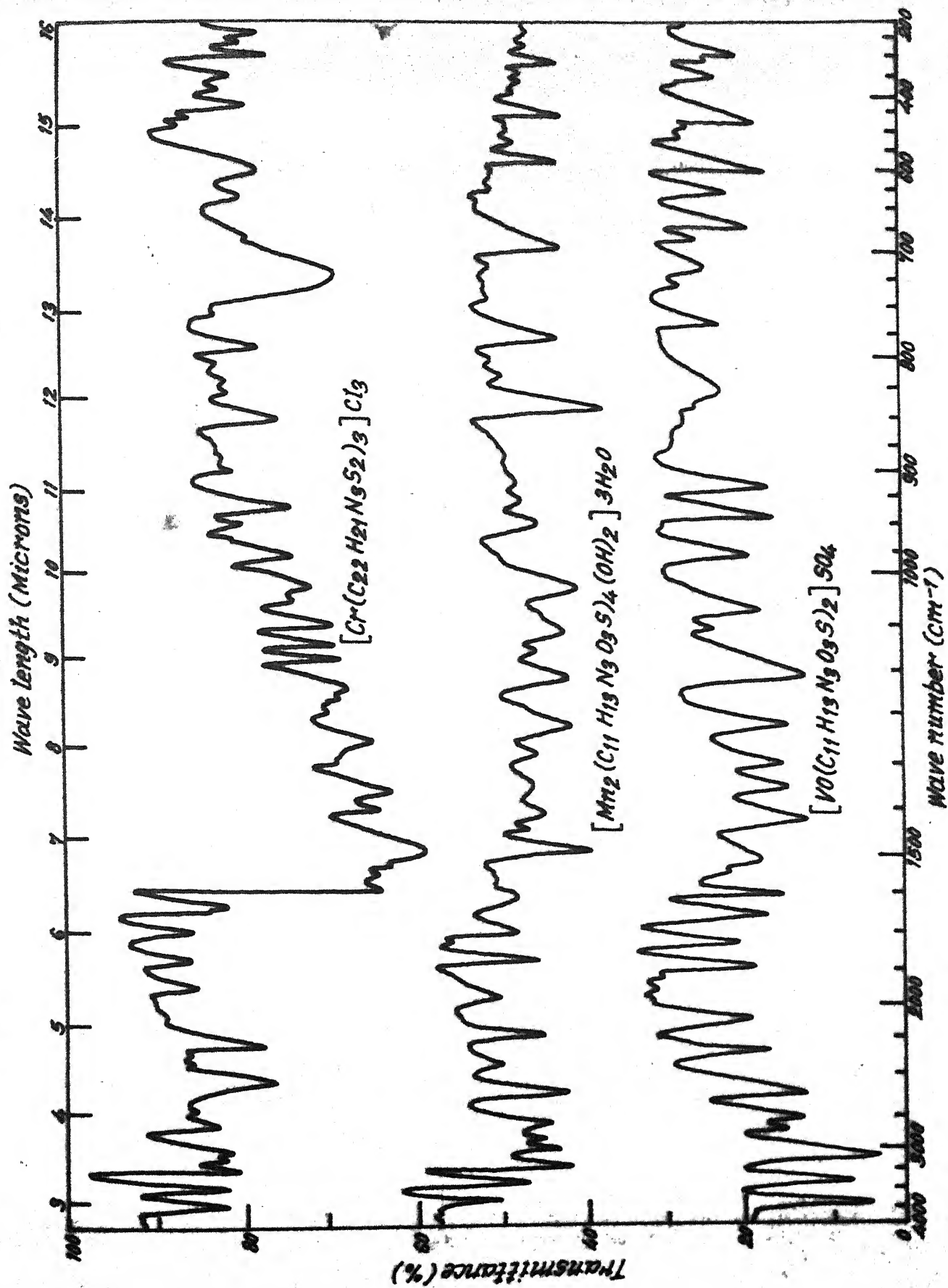
Fig. (7.1) : I.R. Spectra of Cr(III), Mn(III), VO(IV) complexes.

at 1350 and 1320 cm-1. By comparing the spectra of the complexes with free ligand, decreased in frequency of >C=O has been observed showing the chelation through carbonyl moiety(66-67).

The free ligand exhibits bands at 3240(S), 3180(S) and 810(MS) cm-1 in its IR spectrum, attributable to ν(NH2) and γ(C=S) respectively. These bands are shifted to lower wave numbers in the spectra of the complexes indicating the coordination from amino nitrogen and thioketo sulphur. From the above discussion it may be concluded that the coordinating sites are >C=O, -CH=N and >C=S (C19H20N2O3S2); -OH, >C=O, -CH=N and >C=S (C18H16N2O4S2) and -NH2, >C=N- and >C=S (C22H21N3S2).

Mn(III) and Co(III) complexes:- The bands observed in the IR spectra of present Mn(III) and Co(III) complexes at 1635, 1690 and 805 cm-1 are assigned to (CH=N); (>C=O) and γ(C=S) modes respectively(68-70). A negative shift of (CH=N) of 30-35 cm-1 in all the complexes indicate the participation of azomethine nitrogen in coordination(71). The carbonyl group band at 1690 cm-1 is shifted to lower wave number in the complex spectrum which suggest the participation of this group, in chelation. However the position of >C=S does not change indicating the non participation of this group in chelation, A non ligand band in the region 820-830 cm-1 assignable to rocking mode of coordinated water. The bands occuring around 400 cm-1 in the spectra of the complexes are assigned to γ(M-S) and ν(M-N) modes(72).

The bands due to $\nu_{as(NH)}$, $\nu_{(NH)}$ and $\nu_{(NH2)}$ either remain unchanged or show a slight positive shift in all the complexes indicating that the $\nu_{(N-H)}$ nitrogen is not involved in bonding. On the basis of above information it may be said that the ligand is bidentate with >C=O and -CH=N coordinating sites.

VO(II) complexes:- The IR spectrum of (C11H13N3O3S) show three bands at 1635; 1690 and 805 cm-1 assignable to $\nu_{(CH=N)}$; >C=O and >C=S groups. The bands around 3400 and 3100 cm-1 assignable to as NH2 and ν_{s} NH2 respectively. The $\nu_{(C=S)}$ band at 805 cm-1 does not shift on complex formation, revealing its non participation in complexation(73).

The band at 1690 cm-1 corresponds to the $\nu_{(C=O)}$ modes(74 - 75) reduced to lower frequency in chelation. This indicate that the oxygen atom of the carbonyl group of the ligand coordinated to the metal ion.

A strong band seen at 1635 cm-1 due to $\nu_{(CH=N)}$ mode(76) in the spectra of ligand is shifted to about 1600 cm-1 after complexation indicating the coordination of azomethine nitrogen to vanadyl ion. A shoulder in the region 1410-1390 cm-1 in the complexes is assigned to the (C-H) deformation mode.

A strong band in the complex was observed at 980 cm-1 which is assigned(77-78) to (v=o). New bands observed in the region 610-450 cm-1 (79-80) are assigned to $\nu_{(M-N)}$ and $\nu_{(M-O)}$ modes(81-85).

From the IR studies of the complex it is presumed that the ligand (C11H13N3O3S) behaves in a bidentate manner coordinating through the (-CH=N) and >C=O groups(86-91).

REFERENCES

CHAPTER - VII

1. J.C. Dabarowick et.al -Biochem. Biophys. Acta (1979) 517.

2. J.T. Garbutt et.al - J. Agric. Food Chem. (1961) 9, 285.

3. E.D. Weinberg - Bacterial Rev. (1957) 21,46.

4. L.J. Boncher and M.O. Ferrel - Jour. Inorg. Nucl. Chem. 35 (1973), 3731.

5. J.P. Tandon - J. Ind. Chem. Soc. 63, 451 (1986).

6. S.F.A. Kettle - coordination compounds- Thomas Nelson and sons, London (1976) PP 168.

7. S.S. Dodwad and S.S. Prabhu - J. Ind. Chem. Soc. 63, 475 (1986), 61, 595 (1984); 60, 546 (1983).

8. C.P. Trivedi, Renu Vyas, Deepali Jain and Purnima Kapoor -J. Ind. Chem. Soc. 67 (1990) 871.

9. K.M. Daoud et.al - J. Ind. Chem. Soc. 67 (1990) 869.

10. W.J. Geary - Coord. Chem. Rev. (1971) 7, 81.

11. A.L. Crumblis and F. Basolo -J. Am. Chem. Soc.(1970)92,55.

12. P.R. Ashton et.al - Inorg. Chim. Acta (1988) 146,99.

13. M.J. Eapen et.al - Jour. Ind. Chem. Soc. 67(1990) 892.

14. I.S. Bryan and J.C. Dabrowiak -Inorg. Chem. 14, 296 (1975).

15. D.R. Neves, and J.C. Dabrowiak - Inorg. Chem. 15, 129(1976).

16. L.J. Boucher - Coord. Chem. Rev. 7, 289 (1972).

17. R.H. Holm, G.W. Everett, Jr. and A. Chakravorty - prog. Inorg. Chem . (1966), 7, 83, 14, 241 (1971).

18. S. Yamada - Coord. Chem. Rev. (1966), 1, 415, (1967), 2, 83.

19. M.A. Ali and S.E. Livingstone -Coord. Chem. Rev. (1974), 13, 101.

20. V. Casellato, M. Vidali and P.A. Vigato - Coord. Chem. Rev. (1977), 23, 31.

21.(a) M.C. Golonka and A. Bartecki - Coord. Chem. Rev. (1979),31, 251.

(b) H. Green - talanta 1964, 11, 1561, (1973) 20, 139.

22. E. Konig - Inorg. Chem. 10 (1971) 2632.

23. C.K. Jorgensen - Jour. Inorg. Nucl. Chem. 24(1962) 1571.

24. M.A. Sawant and S.M. Khopkar - Talanta (1980), 27, 209.

25. C.L. Sharma, R.S. Arya and S.S. Narvi - J. Ind. Chem. Soc. 63, 267 (1986).

26. A.B.P. Lever - Coord. Chem. Rev. 3, 119 (1968).

27. D.W. Barnum -Jour. Inorg. Nucl. Chem. 21 (1961) 221, 22 (1962), 183.

28. B.N. Figgis - "Introduction to ligand fields" - John Wiley and Sons, N.Y. (1968), PP. 216, 223-315.

29.(a) E. Konig - Struct Bonding (1971) 9, 175.

(b) R.K. Das and P.C. Roy - J. Ind. Chem. Soc. 67(1990) 896.

30.(a) J.R. Perumareddi - Z. Naturforrsch 22 (1967) 908.

(b) M. Abraham and P.K. Radha Krishnan - Jour. Ind. Chem. Soc. 67 (1990) 900.

31. G.M. Cole and B.B. Garret - Inorg. Chem. 2(1970) 1898.

32. A.B.P. Lever and J.C. Hampd - Prog. Inorg. Chem. 22(1976) 255.

33.(a) C.L. Sharma, T.K. De and P.K. Jain - Chem. Scr;(1981),18,79.

   (b) M.P. Suh, S.G. Kang, V.L. Goedken and S.M. Park - Inorg. Chem. 30(1991) 365.

34.(a) A.B.P. Lever - Inorganic electronic spectroscopy - Elesevier Amsterdam (1968).

   (b) A.Mc Auley and S. Subramaniam - Inorg. Chem. 30(1991)371.

35.   R.P. Stanley and A.E. Martell - Coord. Chem. Rev. 19(1980) 15.

36.   J.R. Perumareddi - Coord. Chem. Rev. 4, 73(1969).

37.   P.B. Ashton and D.E. Fenton - Inorg. Chim. Acta (1988) 146,99.

38.   C.J. Ballhausen -"Introduction to ligand field theory" - McGraw Hill, New York, N.Y. (1962).

39.   R.H. Simovi - J. Phys. Chem. (1986) 90, 2802.

40.   I.H. Ahuja and R. Singh - J. Inorg. Nucl. Chem. (1973) 35, 561.

41.   A.B.P. Lever - Coord. Chem. Rev. 3, 119 (1968).

42.   W.T. Geary - Coord. Chem. Rev. (1971) 7, 81:

43.   A.B.P. Lever and J.C. Hempd - Prog. Inorg. Chem. 22(1976) 255.

44.   R.C. Paul, N.C. Sharma, R.D. Verma and A.K. Sharma - Ind. Jour. Chem. 14 A (1976) 705.

45.   D.R. Neves and J.C. Dabrowiak - Inorg. Chem. 15, 129 (1976).

46.   M.L. Ellzey - J. Chem. Phys.- 57, 1796 (1972).

47.   W. Levason and C.A. Masuliffe - Coord. Chem. Rev. 7(1971), 377.

48.　　M.R.G.　Nair and C.P. Prabhakaran - J. Inorg. Nucl. Chem (1981) 43,3390.

49.　　V.W. Day, B.R. Stults, E.L. Tasset, R.O. Day and R.S. Marianelli - J. Am. Chem. Soc. 96, 2650(1974).

50.　　T.S. Davies, J.P. Fackler and M.J. Weeks - Inorg. Chem. 7, 1994 (1961).

51.　　C. Furlani, C. Bellitoo and A.A.G. Tomlinson - J. Chem. Soc.(A) 3267(1971).

52.　　B.R. Stults, V.W. Day, E.L. Tasset, and R.S. Marianelli Inorg. Nucl. Chem. Letters 9, 1259 (1973).

53.　　D.P.Garaddon - Coord. chem. Rev:(1969) 4, 1.

54.　　J.Selbin - Jour. chem. Edu 41 (1964) 86.

55.　　A.K.Day , K.K.Chatterjee and S.K.Sen - Jour. Ind. chem. Soc. 50 (1973), 1689.

56.　　M.J.M.Campbell, A.J.Collins and R.Grzeskowiask - Jour. Inorg. ucl. chem. 38 (1976) 173.

57.　　L.G.Vanquickenborne and S.P.Moglynn - Theo-chim. Acta

58.　　M.D.Munkir Hossain - J. Ind. chem. Soc. 67 (1990) 664.

59.　　J. Selbin and L.Morpurgo - J. inorg. nucl. chem. (1965)27,673.

60.　　H.J.Stoklosa,J.R. Wasson and B.J.Mccormick -Inorg. chem. 13 (1974)592.587

61.　　E. Sinn - Coord . chem. Rev. (1970) 5, 313.

62.　　P.L.Maurya, B.V.Agarwal and A.K. Dey- Polym. Bull (1979),1,631.

63.　　V.J. Babar,d.v. Khansmis and V.M.Shinder- J.Ind.Chem.soc.(1981)58,970.

64. M.M.Mostafa,A.M.Shallaby and A.A.EI-Asmy- J.inorg. nucl. chem. (1981), 43 2992.

65. B.Dash and S.K.Mahapatra- J.inorg. Nucl. chem.(1975),37,

66. U.C. Agarwal and J.S.Dwivedi.J.Inorg.nucl.chem.(1973)35 ,2229.

67. Jyoti Sharma, H.B. Singh and T.Sundersena Rao - Ind. Jour. chemistry 25A,330 (1986).

68. M.C.Jain R.K. Sharma and P.C.Jain J.Inorg.nucl chem.(1984)42,1229.

69. C.A.Tsipis and G.E.Manoussakis - Inorg. Chim Acta 18(1976)35.

70. D.C.Bradley and G.E. Gitlitz-J.chem.soc.(A.)(1969)1152.

71. M.M. Patel,M.R.Patel,M.N.Patel and P.R.Patel- Ind. J. Chem.20 A, (1981),623.

72. M.H.Sonar and A.S.R.Murty- J. Inorg. nucl. chem. (1977) 39,2155.

73. S.N. Podder and N.J. Saha- J.ind. chem. SOC. 52 (1975), 57.

74. H.K.Gupta,P.L. Maurya and A.K.Dey- J.Ind.chem .soc 59 (1982)216.

75. N.S. Viradar, B.R. Patil,and V.H.Kulkarni - J.Inorg.nucl chem. 37 (1975)Synth. React. Inorg. Met. Org.Chem. 14 (1984),773. Ind. j. Chem. 23A (1984)586.

76. B.Samuel,R.Snaith, C.Sommerford and K.Wade - J.chem.Soc. (A) (1970) 1029.

77. S.Pahye - Coord . chem. Rev. (1985) 63, 127.

78. A.N.Speca , N.M.Karayanis and L.L. Pytlewski - Inorg. chim. Acta 9 (1974), 87.

79. B.Beerof, M.J.M.Campbell and K.Crezeskowiak - J. inorg. Nucl. chem. 36 (1974) 87.

80. K.L.Jaura, S.K.Bhalla, B.D.Gupta and V.K.Verma - Ind. J. chem. (1973) 11, 49.

81. Ulrich, Heinzel and Raimer Mattes Polyhedron - 10 (1991) PP 19-25.

82. W.V.Zhongzhi and Zhogwen - Polyhedron 10 (1991) 31.

83. C.F.Edwards and W.P. Griffith Polyhedron 10 (1991) 61.

84. J.C.Beamish, A;an Bordman and I.J.Worrall - Polyhedron 10 (1991) 95.

85. G.S.Sanyal and S. Garad - Ind. J. chem. 30 A (1991) 375.

86. A.A.M.Maly and A.H.Osman - Ind -J - chem. 30A (1991) 379.

87. R.D.Adams, T.A.Wolfe and W.UU- Polyhedron 10 (1991) 447.

88. H.K.Shin, M.J.Hampden smith , E.N.Dulsler and T.T. Kodas Polyhedron 10 (1991) 645.

89. R.T.Streeper and Sadeghkhazelli- Polyhedron 10 (1991) 221.

90. R.D.Fischer and Li King Lu- J.Less Common metals (1985) 78, 42.

91. R.Uson etal - J. chem. Soc. Dalton Trans (1990) 151.

CHAPTER - VIII

Biocidal activity of some compound

Introduction   :- The year 1934 may be regarded as the opening area of organic sulphur pesticides with the introduction of Dithiocarbamates. Since then, organic pesticides have assumed an increasing importance. They after the advantage of a greater specificity of action and in many cases lower toxicity to other forms a life . In agriculture , these are of particular value on high quality crops where the added expenses on their use are compensated by the superior quality and often quantity of the final produce. They have also found wide application in industry.

The possibility of designing organic molecule with superior pesticidal activity greater margin of safety for use in agriculture and less hazards led to the rapid pareliminary evaluation of thousand of organic (1-5) compounds for their pesticidal activity sulphur and a number of its organic compounds function as a good fungicides and pesticides . Young and ong studied the preparation and properies of colloidal sulphur as insecticides (6-9) Hydrophobic and hydrophilic sulphur were prepared.

Roork and Busbey have prepared a list of organic sulphur compounds used as pesticides which includes thiocabamates, dithiocarbamates, mercaptans sulphides both aliphatic and aromatic , oxygenated sulphur compounds such as sulphonic acids sulphochlorides, sulphones, sulphoxides , sulphites and sulphates, sulphonamides, thiazines and thiazoles, thioacids, (10-14) thiophenes, thiourea and xanthate.

The group $\underset{\underset{S}{\overset{||}{}}}{>}$ N C — is considered to be essential for

pesticidal action. The hydrogen attached to nitrogen atom may be replaced by alkyl or aryl radicals while the hydrogen attached to sulphur is dissociable and may be replaced by a metal or any salt for ming organic or inorganic radicals.

There is a corelation between the toxicity of metals and their ability to form stable chelates. Following orderof chelate stability and the toxicity of metals prove it;-

Chelate stability : Hg > cd> Ni > Pb >Co = Zn > Ca > Fe > Mn

Toxicity Hg > cd > Ni > Pb > Co > Zn > Fe > Ca

In view of the known toxicity of metal complexes a few metallic 2:5 Dimethoxy Phenyl glyoxal thiosemicarbazone , 4 $-\beta-$ methoxy phenyl thiosemicarbazone of 2:5 Dimothoxy Phenyl glyoxal and Xα-N- methyl S - Benzyl $-\beta$ - N- (2:5 - Dimethoxy phenyl glyoxal) mnethylene dithiocarbazate, have been treated with aqous / ethanolic solution of salts of mercury , Zinc Copper, Cobalt , Manganese, Nickel and ferric and the corresponding complexes have been obtained. All of them have been analysed characterised and tested against As per gillus niger and Altarnaria Solani.

A few complexes have been found very effective against both the test fungi.

A comparison of toxicities of the compounds (Table No.8.1 to 8.3) show that in general 4 $-\beta-$ methoxy Phenyl thiosemicarbazone of 2:5 Dimethoxy phenyl glyoxal is more active than the 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone and α - N - methyl -S- Benzyl $-\beta$ - N- (2:5 Dimethoxy phenyl glyoxal)

methylene dithiocarbazate.

Effect of the metal ions:-

A study of the toxicity of the complexes (Table No. 8.1 to 8.3) show the effect of metals ions on the toxicity in the following order :-

Hg > Ni > Fe > Mn > Zn > Cu for Asper gillus miger

Mg > Cu > Co > Ni> Zn > Mn > Fe for Alternaria Solani

The Hg - Complexes have been found to be the most toxic for both the test fungi.

The toxicities of all the metal complexes have been described in the table on the following pages

Table (8.1) Pesticidal activity of metallic 4-p- methoxy-penyl thiosemicarbazone of 2:5 Dimethoxy phenyl glyoxal   P. No. 175

Radial growth of the fungus colonies in mm

S.No.	M	As per gillus niger				Alternaria Solani			
		Concentration in ppm							
		1000	100	10	0	1000	100	10	0
1	Hg	0	0	20	80	0	0	22	62
2	Cu	0	38	61	80	0	8	17	62
3	Zn	0	15	75	74	0	15	30	74
4	Co	5	37	76	74	0	11	21	74
5	Mn	0	10	60	74	0	17	32	74
6	Ni	0	0	31	74	0	15	42	74
7	Fe	0	5	38	74	0	28	59	74

Table (8.2) Pesticidal activity of
of 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone   P.No.176

Radial growth of the fungus colonies in mm

S.No.   M   As per gillus niger   Alternaria Solani

Concentration in ppm

S.No.	M	1000	100	10	0	1000	100	10	0
1	Hg	0	5	25	54	0	17	32	60
2	Cu	0	0	31	54	0	8	35	60
3	Zn	0	11	55	67	0	12	47	56
4	Co	10	29	61	67	0	4	41	56
5	Mn	0	0	17	67	0	0	42	56
6	Ni	0	5	15	67	0	0	32	56
7	Fe	6	18	58	67	0	15	30	56

Table (8.3) Pesticidal activity of metalic (α-N-methyl-S-Benzyl
-β- N (2:5 Dimethoxy phenyl glyoxal) methylene dithiocarbazate

P. No. 177

Radial growth of the fungus colonies in mm

Concentration in ppm

S.No.	M	As per gillus niger				Alternaria Solani			
		1000	100	10	0	1000	100	10	0
1	Hg	0	0	28	56	0	0	8	70
2	Cu	0	0	33	56	0	10	39	70
3	Zn	0	0	22	63	0	10	50	74
4	Co	6	30	56	63	0	18	35	74
5	Mn	9	39	65	63	0	32	67	74
6	Ni	0	0	15	63	0	0	15	74
7	Fe	20	31	60	63	0	38	58	74

<u>Experimental</u>

<u>Evaluation of the Pesticidal activity</u>

(1) Preparation of the culture media :- 400 ml of water and 400 gm of thinly cut pieces of peeled potatoes were taken in 1000 ml. beaker, In another beaker 15 gms. agar - agar and 350 ml. of water were taken. Both the beakers were heated to boiling in an auto clave or 10-15 lbs pressure for about an half hour.The contents were filtered separately while hot and then mixed in one litre measuring flask contaning 25 gms of dextrose and 60 ml of water. The contents were well stirred for 15 minutes and then the volume was made upto the mark by adding hot water. The media is poured in 250 ml conical flasks and the flasks were plugged with cotton the flasks were then sterilised at 15 lbs pressure for 20 minutes in an autoclave and taken to a sterilised chamber.

(ii)<u>Testing of the toxicity of the compound</u>:-

Four conical flasks of 250 ml capacity were taken and 100 ml of potato - dextrose - agar agar media was poured into each flask. These were plugged with coton and sterilised at 15 lbs pressure for 20 minutes in an auto clave , the flasks were then cooled to 50 C and numbered as 1,2,3,and 4. A 20,000 ppm solution of the test compound was prepared and 5 ml. 0.5 ml and 0.05 ml of it was added in flasks No 1,2, and 3 respectively, giving the final strength of the compound in the media as 1000, 100 and 10 ppm. Flask No 4 represented the zero concentrations of the test compound. The media from each flask was poured as ceptically in four sterilised and numbered petri dishes. These were allowed to cool and as soon as the agar-agar Jelly was set. The dishes were in verted and kept overnight.

(iii) <u>Inoculation</u> <u>of</u> <u>the</u> <u>micro</u> <u>organism</u>:- Seven days old cultures of <u>Alternaria</u> <u>Solani</u> <u>and</u> <u>Aspergillus</u> <u>niger</u> were cut in discs of 0.5 mm. These fungal discs were inoculated in the petri dishes aseptically in a sterilised chamber and were kept for seven days in an incubation chamber at 25 + 1 C.

(iv)<u>Measurement</u> <u>of</u> <u>the</u> <u>fungal</u> <u>growth</u>:- Seven days after the inoculation of the fungi the radial growth of the fungal colony in each petri dishes was measured for each concentration and the average was calculated. The radial growth of the fungal colony in the dish containing zero concentraion of the test compound served as the check.

The results obtained have been described in table Nos. 8.1 to 8.3.

REFERENCES

1. Friese etal - chem. abstr. 86, 11 6684 p (1977).

2. Comanita etal - Bull Insi. Politec. Iasi. 20,1 ,101,(1974).

3. N.K.Kaushik etal - Acta cienc, Indica 4 (1), 26 (1978)

4. Yakuta Sadosiro etal - chem. Abstr. 82 , 15, 94211 n (1975)

5. Promist Tovarov - etal - chem. abstr. 7,532 45q (1980)

6. H.C.Young-Ann. Mo. Bot. Card ,9:403-435 (1922)

7. E.R.deong J. Eco. Evtomol. 17: 533-538 (1924).

8. Oden, Sven - Z. Chem. ind. Kolloids, 8; 186- 193 (1911)

9. L.E.Tisdale - Ann Mo. Bot. Gard 12: 381 -418 (1925).

10. R.C.Roark and R.L.Busbey - USDA, Bur. entonqol. Plant quar antine E-344 (1935).

11. Campbell etal - J.Econ. Evtomol. 27 , 1176-85 (1934)

12. C.H. Richardson and C.R.Smith USDA Bull. 1160 (1923)

13. Ibid- J.Agric Res. 33, 587-609 (1926).

14 F.Tetrasfield and A.W.R.Roberts - J Agric Sci. 10 (1920) 199- 232.

LIST OF PUBLICATIONS

1. Spectral and Magnetic studies of Co (II) Complexes.
   Orient. J. Chem. 6 (1990) 69.

2. Preparation and Characterisation of some new schiff Bases
   - Curr. Sci. (Submitted for publication).

3. Physico chemical studies on High spin octahedral Iron
   (III) complexes - Jour. Ind. Chem. Soc.
   (Submitted for publication)

4. Stereo chemical studies on octahedral and Square planar
   complexes of heavy metal ions with Schiff bases.
   Jour Ind. chem. Soc. (Submitted for publication).

5. Magnetic vis - a - vis Nephelanxetic effect on some Ni
   (II) and Co(II) complexes- Jour. Ind. chem. Soc.
   (Submitted for publication).

6. Stereo chemical behaviour of Trivalent metal ion complexes
   of Schiff bases- Jour. Ind. chem. Soc.
   (Submitted for publication).

7. Studies of coordination compounds of Thiosemicarbazone -
   Ind. J. chem. (Sent for publication).

8. Studies on Biocidal activity of some compound. Curr. Sci.
   (Submitted for publication).